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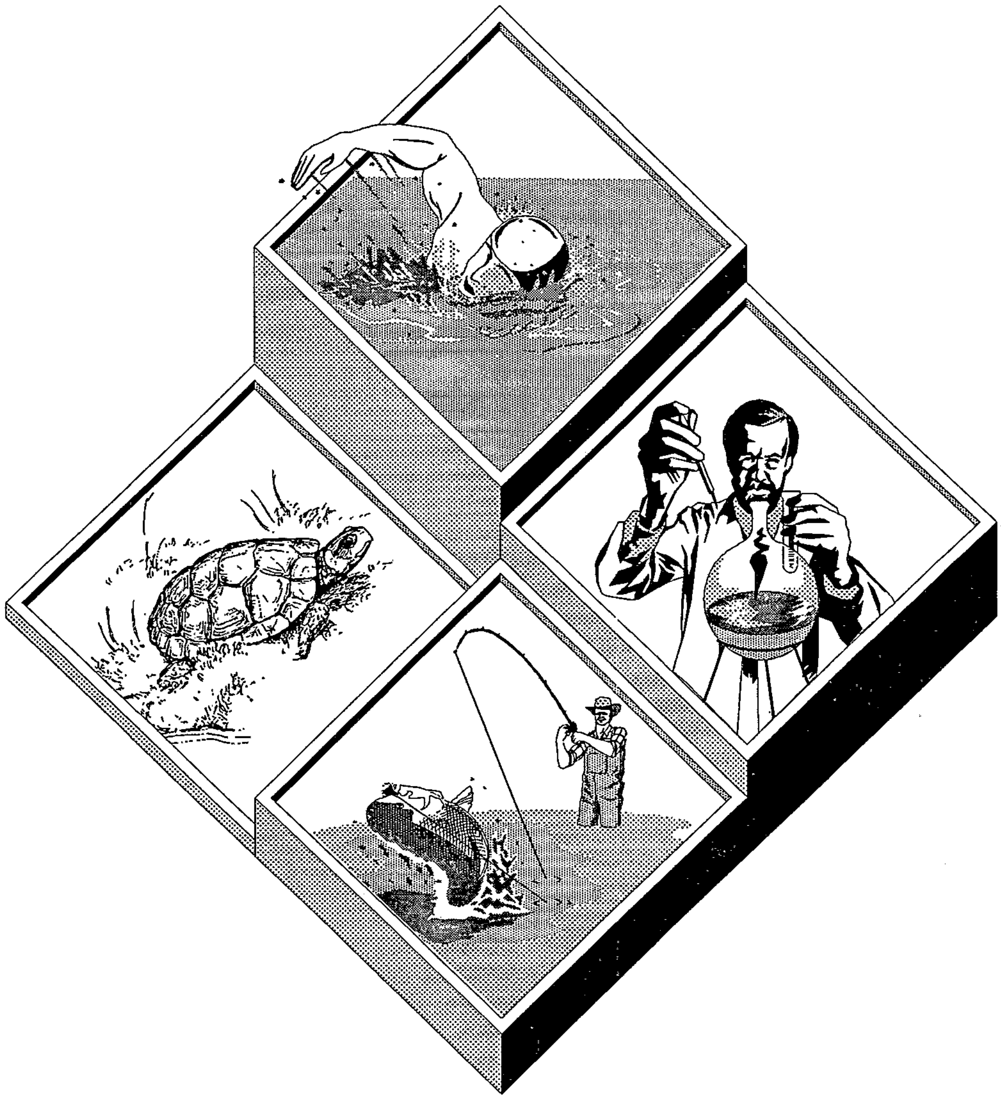
Water Quality Standards Handbook:

Second Edition



"... to restore and maintain the chemical, physical, and biological integrity of the Nation's waters."

Section 101(a) of the Clean Water Act

Contains Update #1
August 1994

WATER QUALITY STANDARDS

HANDBOOK

SECOND EDITION

Water Quality Standards Branch
Office of Science and Technology
U.S. Environmental Protection Agency
Washington, DC 20460

September 1993

Contains update #1
August 1994

FOREWORD

Dear Colleague:

The following document entitled *Water Quality Standards Handbook - Second Edition* provides guidance issued in support of the Water Quality Standards Regulation (40 CFR 131, as amended). This Handbook includes the operative provisions of the first volume of the Handbook issued in 1983 and incorporates subsequent guidance issued since 1983. The 1993 Handbook contains only final guidance previously issued by EPA—it contains no new guidance.

Since the 1983 Handbook has not been updated in ten years, we hope that this edition will prove valuable by pulling together current program guidance and providing a coherent document as a foundation for State and Tribal water quality standards programs. The Handbook also presents some of the evolving program concepts designed to reduce human and ecological risks, such as endangered species protection; criteria to protect wildlife, wetlands, and sediment quality; biological criteria to better define desired biological communities in aquatic ecosystems; and nutrient criteria.

This Handbook is intended to serve as a "living document," subject to future revisions as the water quality standards program moves forward, and to reflect the needs and experiences of EPA and the States. To this end, the Handbook is published in a loose leaf format designed to be placed in three ring binders. This copy of the Handbook includes updated material for 1994 (see Appendix X), and EPA anticipates publishing additional changes periodically and providing them to Handbook recipients. To ensure that you will receive these updates, please copy the reader response card in Appendix W and mail it to the address on the reverse.

The Handbook also contains a listing, by title and date, of the guidance issued since the Handbook was first published in 1983 that is incorporated in the Second Edition. Copies of these documents are available upon request.

The *Water Quality Standards Handbook - Second Edition* provides guidance on the national water quality standards program. EPA regional offices and States may have additional guidance that provides more detail on selected topics of regional interest. For information on regional or State guidance, contact the appropriate regional water quality standards coordinator listed in Appendix U.

EPA invites participation from interested parties in the water quality standards program, and appreciates questions on this guidance as well as suggestions and comments for improvement. Questions or comments may be directed to the EPA regional water quality standards coordinators or to:

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Betsy Southerland, Acting Director
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Note to the Reader

The Water Quality Standards Handbook, first issued in 1983, is a compilation of EPA's guidance on the water quality standards program and provides direction for States in reviewing, revising and implementing water quality standards. The *Water Quality Standards Handbook - Second Edition* retains all the guidance in the 1983 Handbook unless such guidance was specifically revised in subsequent years. An annotated list of the major guidance and policy documents on the water quality standards program issued since 1983 is included in the Introduction and material added to the Second Edition by periodic updates since 1993 is summarized in Appendix X. Material in the Handbook contains only guidance previously issued by EPA; it contains no new guidance.

The guidance contained in each of the documents listed in the Introduction is either: 1) incorporated in its entirety, or summarized, in the text of the appropriate section of this Handbook, or 2) attached as an appendix (see Table of Contents). If there is uncertainty or perceived inconsistency on any of the guidance incorporated into this Handbook, the reader is directed to review the original guidance documents or call the Water Quality Standards Branch at (202) 260-1315. Copies of all original guidance documents not attached as appendices may be obtained from the source listed for each document in the Reference section of this Handbook.

Limited free copies of this Handbook may be obtained from:

Office of Water Resource Center, RC-4100
U. S. Environmental Protection Agency
401 M Street, S.W.
Washington, DC 20460
Telephone: (202) 260-7786 (voice mail publication request line)

Copies may also be obtained from:

Education Resource Information Center/Clearinghouse for Science, Mathematics and Environmental Education (ERIC)
1929 Kenny Road
Columbus, OH 43210-1080 (Telephone: 614-292-6717)
(VISA, Mastercard and purchase order numbers from schools and businesses accepted)

U.S. Department of Commerce
National Technical Information Service (NTIS)
5285 Port Royal Road
Springfield, VA 22161 (Telephone: 1-800-553-6847)
(American Express, VISA and Mastercard accepted)

Robert S. Shippen
Editor

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Appendices:

"Completely mixed condition" is defined as no measurable difference in the concentration of a pollutant exists across a transect of the water body (e.g., does not vary by 5%) (USEPA, 1991a.)

"Criteria" are elements of State water quality standards, expressed as constituent concentrations, levels, or narrative statements, representing a quality of water that supports a particular use. When criteria are met, water quality will generally protect the designated use (40 CFR 131.3.)

"Criteria continuous concentration" (CCC) is the EPA national water quality criteria recommendation for the highest instream concentration of a toxicant or an effluent to which organisms can be exposed indefinitely without causing unacceptable effect (USEPA, 1991a.)

"Criteria maximum concentration" (CMC) is the EPA national water quality criteria recommendation for the highest instream concentration of a toxicant or an effluent to which organisms can be exposed for a brief period of time without causing an acute effect (USEPA, 1991a.)

"Critical life stage" is the period of time in an organism's lifespan in which it is the most susceptible to adverse effects caused by exposure to toxicants, usually during early development (egg, embryo, larvae). Chronic toxicity tests are often run on critical life stages to replace long duration, life cycle tests since the most toxic effect usually occurs during the critical life stage (USEPA, 1991a.)

"Critical species" is a species that is commercially or recreationally important at the site, a species that exists at the site and is listed as threatened or endangered under section 4 of the Endangered Species Act, or a species for which there is evidence that the loss of the species from the site is likely to cause an unacceptable impact on a commercially or recreationally important species, a threatened or endangered species, the abundances of a variety of other species, or the structure or function of the community (USEPA, 1994a.)

"Design flow" is the flow used for steady-state waste load allocation modeling (USEPA, 1991a.)

"Designated uses" are those uses specified in water quality standards for each water body or segment whether or not they are being attained (40 CFR 131.3.)

"Discharge length scale" is the square root of the cross-sectional area of any discharge outlet (USEPA, 1991a.)

"Diversity" is the number and abundance of biological taxa in a specified location (USEPA, 1991a.)

"Effective concentration" (EC) is a point estimate of the toxicant concentration that would cause an observable adverse effect (such as death, immobilization, or serious incapacitation) in a given percentage of the test organisms (USEPA, 1991a.)

"Existing uses" are those uses actually attained in the water body on or after November 28, 1975, whether or not they are included in the water quality standards (40 CFR 131.3.)

"Federal Indian Reservation," "Indian Reservation," or "Reservation" is defined as all land within the limits of any Indian reservation under the jurisdiction of the United States Government, notwithstanding the issuance of any patent, and including rights-of-way running through the reservation (40 CFR 131.3.)

"Final acute value" (FAV) is an estimate of the concentration of the toxicant corresponding to a cumulative probability of 0.05 in the acute toxicity values for all genera for which acceptable acute tests have been conducted on the toxicant (USEPA, 1991a.)

"Frequency" is how often criteria can be exceeded without unacceptably affecting the community (USEPA, 1991a.)

"Harmonic mean flow" is the number of daily flow measurements divided by the sum of the reciprocals of the flows. That is, it is the reciprocal of the mean of reciprocals (USEPA, 1991a.)

"Indian Tribe" or "Tribe" describes any Indian Tribe, band, group, or community recognized by the Secretary of the Interior and exercising governmental authority over a Federal Indian reservation (40 CFR 131.3.)

"Inhibition concentration" (IC) is a point estimate of the toxicant concentration that would cause a given percent reduction (e.g., IC25) in a non-lethal biological measurement of the test organisms, such as reproduction or growth (USEPA, 1991a.)

"Lethal concentration" is the point estimate of the toxicant concentration that would be lethal to a given percentage of the test organisms during a specified period (USEPA, 1991a.)

"Lipophilic" is a high affinity for lipids (fats) (USEPA, 1991a.)

"Load allocations" (LA) the portion of a receiving water TMDL that is attributed either to one of its existing or future nonpoint sources of pollution or to natural background sources (USEPA, 1991a.)

"Lowest-observed-adverse-effect-level" (LOAEL) is the lowest concentration of an effluent or toxicant that results in statistically significant adverse health effects as observed in chronic or subchronic human epidemiology studies or animal exposure (USEPA, 1991a.)

"Magnitude" is how much of a pollutant (or pollutant parameter such as toxicity), expressed as a concentration or toxic unit is allowable (USEPA, 1991a.)

"Minimum level" (ML) refers to the level at which the entire analytical system gives recognizable mass spectra and acceptable calibration points when analyzing for pollutants of concern. This level corresponds to the lowest point at which the calibration curve is determined (USEPA, 1991a.)

"Mixing zone" is an area where an effluent discharge undergoes initial dilution and is extended to cover the secondary mixing in the ambient water body. A mixing zone is an allocated impact zone where water quality criteria can be exceeded as long as acutely toxic conditions are prevented (USEPA, 1991a.)

"Navigable waters" refer to the waters of the United States, including the territorial seas (33 USC 1362.)

"No-observed-adverse-effect-level" (NOAEL) is a tested dose of an effluent or a toxicant below which no adverse biological effects are observed, as identified from chronic or subchronic human epidemiology studies or animal exposure studies (USEPA, 1991a.)

"No-observed-effect-concentration" (NOEC) is the highest tested concentration of an effluent or a toxicant at which no adverse effects are observed on the aquatic test organisms at a specific time of observation. Determined using hypothesis testing (USEPA, 1991a.)

"Nonthreshold effects" are associated with exposure to chemicals that have no safe exposure levels. (i.e., cancer) (USEPA, 1991a.)

"Persistent pollutant" is not subject to decay, degradation, transformation, volatilization, hydrolysis, or photolysis (USEPA, 1991a.)

"Pollution" is defined as the man-made or man-induced alteration of the chemical, physical, biological and radiological integrity of water (33 USC 1362.)

"Priority pollutants" are those pollutants listed by the Administrator under section 307(a) of the Act (USEPA, 1991a.)

"Reference ambient concentration" (RAC) is the concentration of a chemical in water which will not cause adverse impacts to human health; RAC is expressed in units of mg/l (USEPA, 1991a.)

"Reference conditions" describe the characteristics of water body segments least impaired by human activities. As such, reference conditions can be used to describe attainable biological or habitat conditions for water body segments with common watershed/catchment characteristics within defined geographical regions.

"Reference tissue concentration" (RTC) is the concentration of a chemical in edible fish or shellfish tissue which will not cause adverse impacts to human health when ingested. RTC is expressed in units of mg/kg (USEPA, 1991a.)

"Reference dose" (RfD) is an estimate of the daily exposure to human population that is likely to be without appreciable risk of deleterious effect during a lifetime; derived from NOAEL or LOAEL (USEPA, 1991a.)

"Section 304(a) criteria" are developed by EPA under authority of section 304(a) of the Act based on the latest scientific information on the relationship that the effect of a constituent concentration has on particular aquatic species and/or human health. This information is issued periodically to the States as guidance for use in developing criteria (40 CFR 131.3.)

"Site-specific aquatic life criterion" is a water quality criterion for aquatic life that has been derived to be specifically appropriate to the water quality characteristics and/or species composition at a particular location (USEPA, 1994a.)

"States" include: the 50 States, the District of Columbia, Guam, the Commonwealth of Puerto Rico, Virgin Islands, American Samoa, the Trust Territory of the Pacific Islands, and the Commonwealth of the Northern Mariana Islands, and Indian Tribes that EPA determines qualify for treatment as States for the purposes of water quality standards (40 CFR 131.3.)

"Steady-state model" is a fate and transport model that uses constant values of input variables to predict constant values of receiving water quality concentrations (USEPA, 1991a.)

"STORET" is EPA's computerized water quality database that includes physical, chemical, and biological data measured in water bodies throughout the United States (USEPA, 1991a.)

"Sublethal" refers to a stimulus below the level that causes death (USEPA, 1991a.)

"Synergism" is the characteristic property of a mixture of toxicants that exhibits a greater-than-additive total toxic effect (USEPA, 1991a.)

"Threshold effects" result from chemicals that have a safe level (i.e., acute, subacute, or chronic human health effects) (USEPA, 1991a.)

"Total maximum daily load" (TMDL) is the sum of the individual waste load allocations (WLAs) and load allocations (LAs); a margin of safety is included with the two types of allocations so that any additional loading, regardless of source, would not produce a violation of water quality standards (USEPA, 1991a.)

"Toxicity test" is a procedure to determine the toxicity of a chemical or an effluent using living organisms. A toxicity test measures the degree of effect on exposed test organisms of a specific chemical or effluent (USEPA, 1991a.)

"Toxic pollutant" refers to those pollutants, or combination of pollutants, including disease-causing agents, which after discharge and upon exposure, ingestion, inhalation, or assimilation into any organism, either directly from the environment or indirectly by ingestion through food chains, will, or on the basis of information available to the administrator, cause death, disease, behavioral abnormalities, cancer, genetic mutations, physiological malfunctions (including malfunctions in reproduction) or physical deformations, in such organisms or their offspring (33 USC section 1362.)

"Toxic units" (TUs) are a measure of toxicity in an effluent as determined by the acute toxicity units (TUa) or chronic toxicity units (TUc) measured (USEPA, 1991a.)

"Toxic unit acute" (TUa) is the reciprocal of the effluent concentration that causes 50 percent of the organisms to die by the end of the acute exposure period (i.e., $100/LC_{50}$) (USEPA, 1991a.)

"Toxic unit chronic" (TUc) is the reciprocal of the effluent concentration that causes no observable effect on the test organisms by the end of the chronic exposure period (i.e., 100/NOEC) (USEPA, 1991a.)

"Use attainability analysis" (UAA) is a structured scientific assessment of the factors affecting the attainment of the use which may include physical, chemical, biological, and economic factors as described in section 131.10(g) (40 CFR 131.3.)

"Waste load allocation" (WLA) is the portion of a receiving water's TMDL that is allocated to one of its existing or future point sources of pollution (USEPA, 1991a.)

"Waters of the United States" refer to:

(1) all waters which are currently used, were used in the past, or may be susceptible to use in interstate or foreign commerce, including all waters which are subject to the ebb and flow of the tide;

(2) all interstate waters, including interstate wetlands;

(3) all other waters such as intrastate lakes, rivers, streams (including intermittent streams), mudflats, sandflats, wetlands, sloughs, prairie potholes, wet meadows, playa lakes, or natural ponds the use or degradation of which would affect or could affect interstate or foreign commerce, including any such waters:

(i) which are or could be used by interstate or foreign travelers for recreational or other purposes;

(ii) from which fish or shellfish are or could be taken and sold in interstate or foreign commerce; or

(iii) which are or could be used for industrial purposes by industries in interstate commerce.

(4) all impoundments of waters otherwise defined as waters of the United States under this definition;

(5) tributaries of waters in paragraphs (1) through (4) of this definition;

(6) the territorial sea; and

(7) wetlands adjacent to waters (other than waters that are themselves wetlands) identified in paragraphs (1) through (6) of this definition. "Wetlands" are defined as those areas that are inundated or saturated by surface or groundwater at a frequency and duration sufficient to support, and that under normal circumstances do support, a prevalence of vegetation typically adapted for life in saturated soil conditions. Wetlands generally include swamps, marshes, bogs, and similar areas.

Waste treatment systems, including treatment ponds or lagoons designed to meet the requirements of the Act (other than cooling ponds as defined in 40 CFR 423.11(m) which also meet the criteria for this definition) are not waters of the United States. (40 CFR 232.2.)

"Water-effect ratio" (WER) is an appropriate measure of the toxicity of a material obtained in a site water divided by the same measure of the toxicity of the same material obtained simultaneously in a laboratory dilution water (USEPA, 1994a.)

"Water quality assessment" is an evaluation of the condition of a water body using biological surveys, chemical-specific analyses of pollutants in water bodies, and toxicity tests (USEPA, 1991a.)

"Water quality limited segment" refers to any segment where it is known that water quality does not meet applicable water quality standards and/or is not expected to meet applicable water quality standards even after application of technology-based effluent limitations required by sections 301(b)(1)(A) and (B) and 306 of the Act (40 CFR 131.3.)

"Water quality standards" (WQS) are provisions of State or Federal law which consist of a designated use or uses for the waters of the United States, water quality criteria for such waters based upon such uses. Water quality standards are to protect public health or welfare, enhance the quality of the water and serve the purposes of the Act (40 CFR 131.3.)

"Whole-effluent toxicity" is the total toxic effect of an effluent measured directly with a toxicity test (USEPA, 1991a.)

Section 401 certification and FERC licenses (USEPA, 1991h), clarifies the range of water quality standards elements that States need to apply when making CWA section 401 certification decisions. Section 401 of the CWA is discussed in section 7.6.3.

Technical Support Document for Water Quality-based Toxics Control, (USEPA, 1991a), provides technical guidance for assessing and regulating the discharge of toxic substances to the waters of the United States.

Policy on the Use of Biological Assessments and Criteria in the Water Quality Program (USEPA, 1991i), provides the basis for EPA's policy that biological surveys shall be fully integrated with toxicity and chemical-specific assessment methods in State water quality programs. Further discussion of this policy is contained in section 3.3.

Numeric Water Quality Criteria for Wetlands (Appendix E), evaluates EPA's numeric aquatic life criteria to determine how they can be applied to wetlands. Wetland aquatic life criteria are discussed in section 3.5.6.

Endangered Species Act Joint Guidance (Appendix F), establishes a procedure by which EPA, the U.S. Fish and Wildlife Service, and the National Marine Fisheries Service will consult on the development of water quality criteria and standards.

Office of Water Policy and Technical Guidance on Interpretation and Implementation of Aquatic Life Metals Criteria (USEPA, 1993f), transmits Office of Water (OW) policy and guidance on the interpretation and implementation of aquatic life criteria for the management of metals. Section 3.6 discusses EPA's policy on aquatic life metals criteria.

Interpretation of Federal Antidegradation Regulatory Requirement (USEPA, 1994a), provides guidance on the interpretation of the antidegradation policy in 40 CFR 131.12(a)(2) as it relates to nonpoint sources. Antidegradation and nonpoint sources are discussed in Section 4.6.

Interim Guidance on Determination and Use of Water-Effect Ratios for Metals (Appendix L), provides interim guidance concerning the experimental determination of water-effect ratios (WERs) for metals and supersedes all guidance concerning water-effect ratios and the Indicator Species Procedure in USEPA, 1983a and in USEPA, 1984f. It also supersedes the guidance in these earlier documents for the Recalculation Procedure for performing site-specific aquatic life criteria modifications. Site-specific aquatic life criteria are discussed in Section 3.7.

The guidance contained in each of the above documents is either incorporated into the text of the appropriate section of this Handbook or attached as appendices (see Table of Contents). The reader is directed to the original guidance documents for the explicit guidance on the topics discussed. Copies of all original guidance documents not attached as appendices may be obtained from the source listed for each document in the Reference section of this Handbook.

The *Water Quality Standards Handbook - Second Edition* is reorganized from the 1983 Handbook. An overview to Water Quality Standards and Water Quality Management programs has been added, and chapters 1 through 6 are organized to parallel the provisions of the Water Quality Standards Regulation. Chapter 7 briefly introduces the role of water quality standards in the water quality-based approach to pollution control.

The *Water Quality Standards Handbook - Second Edition* retains all the guidance in the 1983 Handbook unless such guidance was specifically revised in subsequent years.

OVERVIEW OF THE WATER QUALITY STANDARDS PROGRAM

A water quality standard defines the water quality goals of a water body, or portion thereof, by designating the use or uses to be made of the water, by setting criteria necessary to protect the uses, and by preventing degradation of water quality through antidegradation provisions. States adopt water quality standards to protect public health or welfare, enhance the quality of water, and serve the purposes of the Clean Water Act.

"Serve the purposes of the Act" (as defined in sections 101(a), 101(a)(2), and 303(c) of the Act) means that water quality standards:

- include provisions for restoring and maintaining chemical, physical, and biological integrity of State waters;
- wherever attainable, achieve a level of water quality that provides for the protection and propagation of fish, shellfish, and wildlife, and recreation in and on the water ("fishable/swimmable"); and
- consider the use and value of State waters for public water supplies, propagation of fish and wildlife, recreation, agriculture and industrial purposes, and navigation.

Section 303(c) of the Clean Water Act provides the statutory basis for the water quality standards program. The regulatory requirements governing the program, the *Water Quality Standards Regulation*, are published at 40 CFR 131. The Regulation is divided into four subparts (A through D), which are summarized below.

General Provisions (40 CFR 131 - Subpart A)

Subpart A includes the scope (section 131.1) and purpose (section 131.2) of the Regulation, definitions of terms used in the Regulation (section 131.3), State (section 131.4) and EPA (section 131.5) authority for water quality standards, and the minimum requirements for a State water quality standards submission (section 131.6).

On December 12, 1991, the EPA promulgated amendments to Subpart A of the Water Quality Standards Regulation in response to the CWA section 518 requirements (see 56 F.R. 64875). The Amendments:

- establish a mechanism to resolve unreasonable consequences that may result from an Indian Tribe and a State adopting differing water quality standards on common bodies of water (section 131.7); and
- add procedures by which an Indian Tribe can qualify for the section 303 water quality standards and section 401 certification programs of the Clean Water Act (section 131.8).

The sections of Subpart A are discussed in chapter 1.

Establishment of Water Quality Standards - (Subpart B)

Subpart B contains regulatory requirements that must be included in State water quality standards: designated uses (section 131.10), criteria that protect the designated uses (section 131.11), and an antidegradation policy that protects existing uses and high water quality (section 131.12). Subpart B also provides for State discretionary policies, such as mixing zones and water quality standards variances (section 131.13).

Each of these sections is summarized below and discussed in detail in chapters 2 through 5 respectively.

Designation of Uses

The Water Quality Standards Regulation requires that States specify appropriate water uses to be

CHAPTER 2

DESIGNATION OF USES

(40 CFR 131.10)

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federally permitted or licensed activities that may result in a discharge to waters of the United States. The decision to grant or to deny certification, or to grant a conditional certification is based on a State's determination regarding whether the proposed activity will comply with applicable water quality standards and other provisions. Thus, States may deny certification and prohibit EPA from issuing an NPDES permit that would violate water quality standards. Section 401 also allows a State to participate in extraterritorial actions that will affect that State's waters if a federally issued permit is involved.

In addition to the above sources for solutions, when the problem arises between a State and an Indian Tribe qualified for treatment as a State for water quality standards, the dispute resolution mechanism could be invoked (see section 1.7, of this Handbook).

2.3 Use Subcategories - 40 CFR 131.10(c)

States are required to designate uses considering, at a minimum, those uses listed in section 303(c) of the Clean Water Act (i.e., public water supplies, propagation of fish and wildlife, recreation, agriculture and industrial purposes, and navigation). However, flexibility inherent in the State process for designating uses allows the development of subcategories of uses within the Act's general categories to refine and clarify specific use classes. Clarification of the use class is particularly helpful when a variety of surface waters with distinct characteristics fit within the same use class, or do not fit well into any category. Determination of non-attainment in waters with broad use categories may be difficult and open to alternative interpretations. If a determination of non-attainment is in dispute, regulatory actions will be difficult to accomplish (USEPA, 1990a).

The State selects the level of specificity it desires for identifying designated uses and subcategories of uses (such as whether to treat recreation as a single use or to define a subcategory for secondary recreation). However, the State must be at least as specific as the uses listed in sections 101(a) and 303(c) of the Clean Water Act.

Subcategories of aquatic life uses may be on the basis of attainable habitat (e.g., coldwater versus warmwater habitat); innate differences in community structure and function (e.g., high versus low species richness or productivity); or fundamental differences in important community components (e.g., warmwater fish communities dominated by bass versus catfish). Special uses may also be designated to protect particularly unique, sensitive, or valuable aquatic species, communities, or habitats.

Data collected from biosurveys as part of a developing biocriteria program may assist States in refining aquatic life use classes by revealing consistent differences among aquatic communities inhabiting different waters of the same designated use. Measurable biological attributes could then be used to divide one class into two or more subcategories (USEPA, 1990a).

If States adopt subcategories that do not require criteria sufficient to fully protect the goal uses in section 101(a)(2) of the Act (see section 2.1, above), a use attainability analysis pursuant to 40 CFR 131.10(j) must be conducted for waters to which these subcategories are assigned. Before adopting subcategories of uses, States must provide notice and opportunity for a public hearing because these actions are changes to the standards.

2.4 Attainability of Uses - 40 CFR 131.10(d)

When designating uses, States may wish to designate only the uses that are attainable. However, if the State does not designate the uses specified in section 101(a)(2) of the Act, the State must perform a use attainability analysis under section 131.10(j) of the regulation. States are encouraged to designate uses that the State believes can be attained in the future.

"Attainable uses" are, at a minimum, the uses (based on the State's system of water use classification) that can be achieved 1) when effluent limits under sections 301(b)(1)(A) and (B) and section 306 of the Act are imposed on point source dischargers and 2) when cost-effective and reasonable best management practices are imposed on nonpoint source dischargers.

2.5 Public Hearing for Changing Uses - 40 CFR 131.10(e)

The Water Quality Standards Regulation requires States to provide opportunity for public hearing before adding or removing a use or establishing subcategories of a use. As mentioned in section 2.2 above, the State should consider extraterritorial effects of such changes.

2.6 Seasonal Uses - 40 CFR 131.10(f)

In some areas of the country, uses are practical only for limited seasons. EPA recognizes seasonal uses in the Water Quality Standards Regulation. States may specify the seasonal uses and criteria protective of that use as well as the time frame for the ". . . season, so long as the criteria do not prevent the attainment of any more restrictive uses attainable in other seasons."

For example, in many northern areas, body contact recreation is possible only a few months out of the year. Several States have adopted primary contact recreational uses, and the associated microbiological criteria, for only those months when primary contact recreation actually occurs, and have relied on less stringent secondary contact recreation criteria to protect for incidental exposure in the "non-swimming" season.

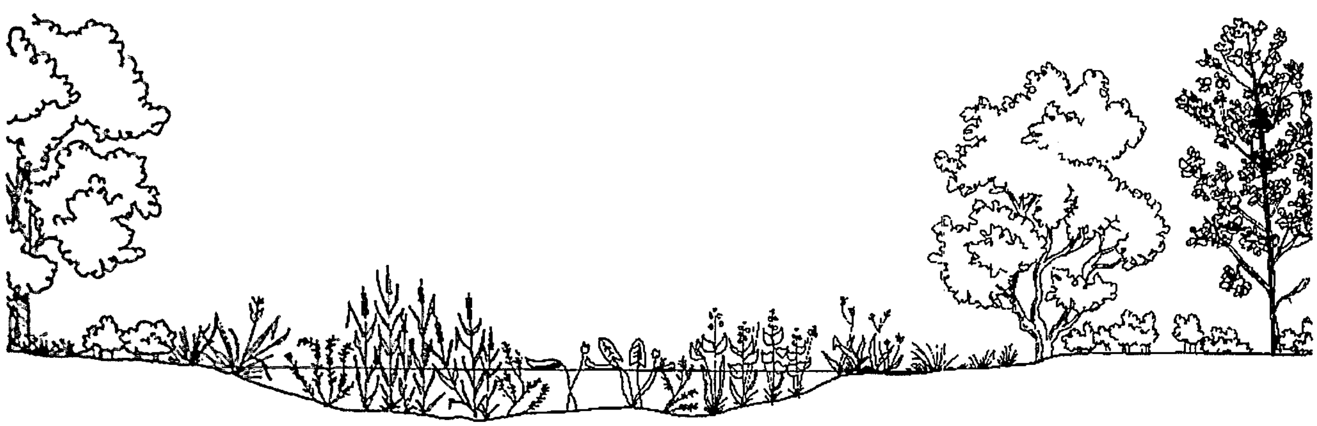
Seasonal uses that may require more stringent criteria are uses that protect sensitive organisms or life stages during a specific season such as the early life stages of fish and/or fish migration (e.g., EPA's *Ambient Water Quality Criteria for Dissolved Oxygen* (see Appendix I) recommends more stringent dissolved oxygen criteria for the early life stages of both coldwater and warmwater fish).

2.7 Removal of Designated Uses - 40 CFR 131.10(g) and (h)

Figure 2-1 shows how and when designated uses may be removed.

2.7.1 Step 1 - Is the Use Existing?

Once a use has been designated for a particular water body or segment, the water body or water body segment cannot be reclassified for a different use except under specific conditions. If a designated use is an existing use (as defined in 40 CFR 131.3) for a particular water body, the existing use cannot be removed unless a use requiring more stringent criteria is added (see



CHAPTER 3

WATER QUALITY CRITERIA

(40 CFR 131.11)

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CHAPTER 3
WATER QUALITY CRITERIA

The term "water quality criteria" has two different definitions under the Clean Water Act (CWA). Under section 304(a), EPA publishes water quality criteria that consist of scientific information regarding concentrations of specific chemicals or levels of parameters in water that protect aquatic life and human health (see section 3.1 of this Handbook). The States may use these contents as the basis for developing enforceable water quality standards. Water quality criteria are also elements of State water quality standards adopted under section 303(c) of the CWA (see sections 3.2 through 3.6 of this Handbook). States are required to adopt water quality criteria that will protect the designated use(s) of a water body. These criteria must be based on sound scientific rationale and must contain sufficient parameters or constituents to protect the designated use.

3.1 EPA Section 304(a) Guidance

EPA and a predecessor agency have produced a series of scientific water quality criteria guidance documents. Early Federal efforts were the "Green Book" (FWPCA, 1968) and the "Red Book" (USEPA, 1976). EPA also sponsored a contract effort that resulted in the "Blue Book" (NAS/NAE, 1973). These early efforts were premised on the use of literature reviews and the collective scientific judgment of Agency and advisory panels. However, when faced with the need to develop criteria for human health as well as aquatic life, the Agency determined that new procedures were necessary. Continued reliance solely on existing scientific literature was deemed inadequate because essential information was not available for many pollutants. EPA scientists developed formal methodologies for establishing scientifically defensible criteria. These were subjected to review by the Agency's Science Advisory Board of outside experts and the public. This effort culminated on November 28, 1980, when the Agency published criteria development guidelines for aquatic life and for human health, along with criteria for 64 toxic pollutants (USEPA, 1980a,b). Since that initial publication, the aquatic life methodology was amended (Appendix H), and additional criteria were proposed for public comment and finalized as Agency criteria guidance. EPA summarized the available criteria information in the "*Gold Book*" (USEPA, 1986a), which is updated from time to time. However, the individual criteria documents (see Appendix I), as updated, are the official guidance documents.

EPA's criteria documents provide a comprehensive toxicological evaluation of each chemical. For toxic pollutants, the documents tabulate the relevant acute and chronic toxicity information for aquatic life and derive the criteria maximum concentrations (acute criteria) and criteria continuous concentrations (chronic criteria) that the Agency recommends to protect aquatic life resources. The methodologies for these processes are described in Appendices H and J and outlined in sections 3.1.2 and 3.1.3 of this Handbook.

3.1.1 State Use of EPA Criteria Documents

EPA's water quality criteria documents are available to assist States in:

- adopting water quality standards that include appropriate numeric water quality criteria;
- interpreting existing water quality standards that include narrative "no toxics in toxic amounts" criteria;

- making listing decisions under section 304(1) of the CWA;

- writing water quality-based NPDES permits and individual control strategies; and

- providing certification under section 401 of the CWA for any Federal permit or license (e.g., EPA-issued NPDES permits, CWA section 404 permits, or Federal Energy Regulatory Commission licenses).

In these situations, States have primary authority to determine the appropriate level to protect human health or welfare (in accordance with section 303(c)(2) of the CWA) for each water body. However, under the Clean Water Act, EPA must also review and approve State water quality standards; section 304(1) listing decisions and draft and final State-issued individual control strategies; and in States where EPA writes NPDES permits, EPA must develop appropriate water quality-based permit limitations. The States and EPA therefore have a strong interest in assuring that the decisions are legally defensible, are based on the best information available, and are subject to full and meaningful public comment and participation. It is very important that each decision be supported by an adequate record. Such a record is critical to meaningful comment, EPA's review of the State's decision, and any subsequent administrative or judicial review.

Any human health criterion for a toxicant is based on at least three interrelated considerations:

- cancer potency or systemic toxicity,

- exposure, and

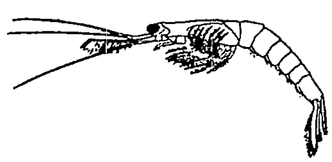
- risk characterization.

States may make their own judgments on each of these factors within reasonable scientific bounds, but documentation to support their judgments, when different from EPA's recommendation, must be clear and in the public record. If a State relies on EPA's section 304(a) criteria document (or other EPA documents), the State may reference and rely on the data in these documents and need not create duplicative or new material for inclusion in their records. However, where site-specific issues arise or the State decides to adopt an approach to any one of these three factors that differs from the approach in EPA's criteria document, the State must explain its reasons in a manner sufficient for a reviewer to determine that the approach chosen is based on sound scientific rationale (40 CFR 131.11(b)).

3.1.2 Criteria for Aquatic Life Protection

The development of national numerical water quality criteria for the protection of aquatic organisms is a complex process that uses information from many areas of aquatic toxicology. (See Appendix H for a detailed discussion of this process.) After a decision is made that a national criterion is needed for a particular material, all available information concerning toxicity to, and bioaccumulation by, aquatic organisms is collected and reviewed for acceptability. If enough acceptable data for 48- to 96-hour toxicity tests on aquatic plants and animals are available, they are used to derive the acute criterion. If sufficient data on the ratio of acute to chronic toxicity concentrations are available, they are used to derive the chronic or long-term exposure criteria. If justified, one or both of the criteria may be related to other water quality characteristics, such as pH, temperature, or hardness. Separate criteria are developed for fresh and salt waters.

The Water Quality Standards Regulation allows States to develop numerical criteria or modify



EPA's recommended criteria to account for site-specific or other scientifically defensible factors. Guidance on modifying national criteria is found in sections 3.6 and 3.7. When a criterion must be developed for a chemical for which a national criterion has not been established, the regulatory authority should refer to the EPA guidelines (Appendix H).

Magnitude for Aquatic Life Criteria

Water quality criteria for aquatic life contain two expressions of allowable magnitude: a criterion maximum concentration (CMC) to protect against acute (short-term) effects; and a criterion continuous concentration (CCC) to protect against chronic (long-term) effects. EPA derives acute criteria from 48- to 96-hour tests of lethality or immobilization. EPA derives chronic criteria from longer term (often greater than 28-day) tests that measure survival, growth, or reproduction. Where appropriate, the calculated criteria may be lowered to be protective ofcomercially or recreationally important species.

Duration for Aquatic Life Criteria

The quality of an ambient water typically varies in response to variations of effluent quality, stream flow, and other factors. Organisms in the receiving water are not experiencing constant, steady exposure but rather are experiencing fluctuating exposures, including periods of high concentrations, which may have adverse effects. Thus, EPA's criteria indicate a time period over which exposure is to be averaged, as well as an upper limit on the average concentration, thereby limiting the duration of exposure to elevated concentrations. For acute criteria, EPA recommends an averaging period of 1 hour. That is, to protect against acute effects, the 1-hour average exposure should not exceed the CMC. For chronic criteria, EPA recommends an averaging period of 4 days. That is, the 4-day average exposure should not exceed the CCC.

Frequency for Aquatic Life Criteria

To predict or ascertain the attainment of criteria, it is necessary to specify the allowable frequency for exceeding the criteria. This is because it is statistically impossible to project that criteria will never be exceeded. As ecological communities are naturally subjected to a series of stresses, the allowable frequency of pollutant stress may be set at a value that does not significantly increase the frequency or severity of all stresses combined.

EPA recommends an average frequency for excursions of both acute and chronic criteria not to exceed once in 3 years. In all cases, the recommended frequency applies to actual ambient concentrations, and excludes the influence of measurement imprecision. EPA established its recommended frequency as part of its guidelines for deriving criteria (Appendix H). EPA selected the 3-year average frequency of criteria exceedence with the intent of providing for ecological recovery from a variety of severe stresses. This return interval is roughly equivalent to a 7Q10 design flow condition. Because of the nature of the ecological recovery studies available, the severity of criteria excursions could not be rigorously related to the resulting ecological impacts. Nevertheless, EPA derives its criteria intending that a single marginal criteria excursion (i.e., a slight excursion over a 1-hour period for acute or over a 4-day period for chronic) would require little or no time for recovery. If the frequency of marginal criteria excursions is not high, it can be shown that the frequency of severe stresses, requiring measurable recovery periods, would be extremely small. EPA thus expects the 3-year return interval to provide a very high degree of protection.

3.1.3 Criteria for Human Health Protection

This section reviews EPA's procedures used to develop assessments of human health effects in developing water quality criteria and reference ambient concentrations. A more complete human health effects discussion is included in the *Guidelines and Methodology Used in the*

Preparation of Health Effects Assessment Chapters of the Consent Decree Water Documents (Appendix J). The procedures contained in this document are used in the development and updating of EPA water quality criteria and may be used in updating State criteria and in developing State criteria for those pollutants lacking EPA human health criteria. The procedures may also be applied as site-specific interpretations of narrative standards and as a basis for permit limits under 40 CFR 122.44 (d)(1)(vi).

Magnitude and Duration

Water quality criteria for human health contain only a single expression of allowable magnitude; a criterion concentration generally to protect against long-term (chronic) human health effects. Currently, national policy and prevailing opinion in the expert community establish that the duration for human health criteria for carcinogens should be derived assuming lifetime exposure, taken to be a 70-year time period. The duration of exposure assumed in deriving criteria for noncarcinogens is more complicated owing to a wide variety of endpoints: some developmental (and thus age-specific and perhaps gender-specific), some lifetime, and some, such as organoleptic effects, not duration-related at all. Thus, appropriate durations depend on the individual noncarcinogenic pollutants and the endpoints or adverse effects being considered.

Human Exposure Considerations

A complete human exposure evaluation for toxic pollutants of concern for bioaccumulation would encompass not only estimates of exposures due to fish consumption but also exposure from background concentrations and other exposure routes, The more important of these include recreational and occupational contact, dietary intake from other than fish, intake from air inhalation, and drinking water consumption. For section 304(a) criteria development, EPA typically considers only exposures to a pollutant that occur through the ingestion of water and contaminated fish and shellfish. This is the exposure default assumption, although the human health guidelines provide for considering other sources where data are available (see 45 F.R. 79354). Thus the criteria are based on an assessment of risks related to the surface water exposure route only (57 F.R. 60862-3).

The consumption of contaminated fish tissue is of serious concern because the presence of even extremely low ambient concentrations of bioaccumulative pollutants (sublethal to aquatic life) in surface waters can result in residue concentrations in fish tissue that can pose a human health risk. Other exposure route information should be considered and incorporated in human exposure evaluations to the extent available.

Levels of actual human exposures from consuming contaminated fish vary depending upon a number of case-specific consumption factors. These factors include type of fish species consumed, type of fish tissue consumed, tissue lipid content, consumption rate and pattern, and food preparation practices. In addition, depending on the spatial variability in the fishery area, the behavior of the fish species, and the point of application of the criterion, the average exposure of fish may be only a small fraction of the expected exposure at the point of application of the criterion. If an effluent attracts fish, the average exposure might be greater than the expected exposure.

With shellfish, such as oysters, snails, and mussels, whole-body tissue consumption commonly occurs, whereas with fish, muscle tissue and roe are most commonly eaten. This difference in the types of tissues consumed has implications for the amount of available bioaccumulative contaminants likely to be ingested. Whole-body shellfish consumption presumably means ingestion of the entire burden of bioaccumulative contaminants. However, with most fish, selective cleaning and removal of internal organs, and sometimes body fat as well, from edible tissues, may result in removal of much of the lipid material in which bioaccumulative contaminants tend to concentrate.

Fish Consumption Values

EPA's human health criteria have assumed a human body weight of 70 kg and the consumption of 6.5 g of fish and shellfish per day. Based on data collected in 1973-74, the national per capita consumption of freshwater and estuarine fish was estimated to average 6.5 g/day. Per capita consumption of all seafood (including marine species) was estimated to average 14.3 g/day. The 95th percentile for consumption of all seafood by individuals over a period of 1 month was estimated to be 42 g/day. The mean lipid content of fish and shellfish tissue consumed in this study was estimated to be 3.0 percent (USEPA, 1980c).

Currently, four levels of fish and shellfish consumption are provided in EPA guidance (USEPA, 1991a):

- 6.5 g/day to represent an estimate of average consumption of fish and shellfish from estuarine and freshwaters by the entire U.S. population. This consumption level is based on the average of both consumers and nonconsumers of.

- 20 g/day to represent an estimate of the average consumption of fish and shellfish from marine, estuarine, and freshwaters by the U.S. population. This average consumption level also includes both consumers and nonconsumers of.

- 165 g/day to represent consumption of fish and shellfish from marine, estuarine, and freshwaters by the 99.9th percentile of the U.S. population consuming the most fish or seafood.

- 180 g/day to represent a "reasonable worst case" based on the assumption that some individuals would consume fishand shellfish at a rate equal to the combined consumption of red meat, poultry, fish, and shellfish in the United States.

EPA is currently updating the national estuarine and freshwater fish and shellfish consumption default values and will provide a range of recommended national consumption values. This range will include:

- mean values appropriate to the population at large; and

- values appropriate for those individuals who consume a relatively large proportion of fish and shellfish in their diets (maximally exposed individuals).

Many States use EPA's 6.5 g/day consumption value. However, some States use the above-mentioned 20 g/day value and, for saltwaters, 37 g/day. In general, EPA recommends that the consumption values used in deriving criteria from the formulas in this chapter reflect the most current, relevant, and/or site-specific information available.

Bioaccumulation Considerations

The ratio of the contaminant concentrations in fish tissue versus that in water is termed either the bioconcentration factor (BCF) or the bioaccumulation factor (BAF). Bioconcentration is defined as involving contaminant uptake from water only (not from food). The bioaccumulation factor (BAF) is defined similarly to the BCF except that it includes contaminant uptake from both water and food. Under laboratory conditions, measurements of tissue/water partitioning are generally considered to involve uptake from water only. On the other hand, both processes are likely to apply in the field since the entire food chain is exposed.

The BAF/BCF ratio ranges from 1 to 100, with the highest ratios applying to organisms in higher trophic levels, and to chemicals with logarithm of the octanol-water partitioning coefficient (log P) close to 6.5.

Bioaccumulation considerations are integrated into the criteria equations by using food chain multipliers (FMs) in conjunction with the BCF. The bioaccumulation and bioconcentration factors for a chemical are related as follows:

$$\mathbf{BAF = FM \times BCF}$$

By incorporating the FM and BCF terms into the criteria equations, bioaccumulation can be addressed.

In Table 3-1, FM values derived from the work of Thomann (1987, 1989) are listed according to log P value and trophic level of the organism. For chemicals with log P values greater than about 7, there is additional uncertainty regarding the degree of bioaccumulation, but generally, trophic level effects appear to decrease due to slow transport kinetics of these chemicals in fish, the growth rate of the fish, and the chemical's relatively low bioavailability. Trophic level 4 organisms are typically the most desirable species for sport fishing and, therefore, FMs for trophic level 4 should generally be used in the equations for calculating criteria. In those very rare situations where only lower trophic level organisms are found, e.g., possibly oyster beds, an FM for a lower trophic level might be considered.

Measured BAFs (especially for those chemicals with log P values above 6.5) reported in the literature should be used when available. To use experimentally measured BAFs in calculating the criterion, the (FM x BCF) term is replaced by the BAF in the equations in the following section. Relatively few BAFs have been measured accurately and reported, and their application to sites other than the specific ecosystem where they were developed is problematic and subject to uncertainty. The option is also available to develop BAFs experimentally, but this will be extremely resource intensive if done on a site-specific basis with all the necessary experimental and quality controls.

	Trophic Levels		
Log P	2	3	4
3.5	1.0	1.0	1.0
3.6	1.0	1.0	1.0
3.7	1.0	1.0	1.0
3.8	1.0	1.0	1.0
3.9	1.0	1.0	1.0
4.0	1.1	1.0	1.0
4.1	1.1	1.1	1.1
4.2	1.1	1.1	1.1
4.3	1.1	1.1	1.1
4.4	1.2	1.1	1.1
4.5	1.2	1.2	1.2
4.6	1.2	1.3	1.3
4.7	1.3	1.4	1.4
4.8	1.4	1.5	1.6
4.9	1.5	1.8	2.0
5.0	1.6	2.1	2.6
5.1	1.7	2.5	3.2
5.2	1.9	3.0	4.3
5.3	2.2	3.7	5.8
5.4	2.4	4.6	8.0
5.5	2.8	5.9	11
5.6	3.3	7.5	16
5.7	3.9	9.8	23
5.8	4.6	13	33
5.9	5.6	17	47
6.0	6.8	21	67
6.1	8.2	25	75
6.2	10	29	84
6.3	13	34	92
6.4	15	39	98
6.5	19	45	100
≥6.5	19.2*	45*	100*

* These recommended FMs are conservative estimates; FMs for log P values greater than 6.5 may range from the values given to as low as 0.1 for contaminants with very low bioavailability.

Table 3-1. Estimated Food Chain Multipliers (FMs)

Updating Human Health Criteria Using IRIS

EPA recommends that States use the most current risk information in the process of updating human health criteria. The Integrated Risk Information System (IRIS) (Barns and Dourson, 1988; Appendix N) is an electronic data base of the USEPA that provides chemical-specific risk information on the relationship between chemical exposure and estimated human health effects. Risk assessment information contained in IRIS, except as specifically noted, has been reviewed and agreed upon by an interdisciplinary group of scientists representing various Program Offices within the Agency and represent an Agency-wide consensus. Risk assessment information and values are updated on a monthly basis and are approved for Agency-wide use. IRIS is intended to make risk assessment information readily available to those individuals who must perform risk assessments and also to increase consistency among risk assessment/risk management decisions.

IRIS contains two types of quantitative risks values: the oral Reference Dose (RfD) and the carcinogenic potency estimate or slope factor. The RfD (formerly known as the acceptable daily intake or ADI) is the human health hazard assessment for noncarcinogenic (target organ) effects. The carcinogenic potency estimate (formerly known as q_1*) represents the upper bound cancer-causing potential resulting from lifetime exposure to a substance. The RfD or the oral carcinogenic potency estimate is used in the derivation of EPA human health criteria.

EPA periodically updates risk assessment information, including RfDs, cancer potency estimates, and related information on contaminant effects, and reports the current information on IRIS. Since IRIS contains the Agency's most recent quantitative risk assessment values, current IRIS values should be used by States in updating or developing new human health criteria. This means that the 1980 human health criteria should be updated with the latest IRIS values. The procedure for deriving an updated human health water quality criterion would require inserting the current Rfd or carcinogenic potency estimate on IRIS into the equations in Exhibit 3.1 or 3.2, as appropriate.

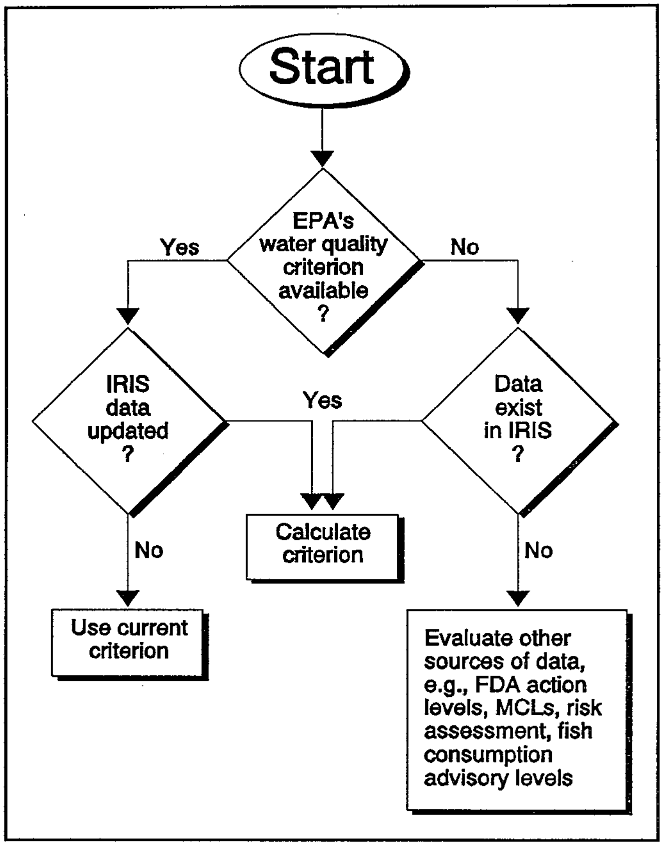


Figure 3-1. Procedure for determining an updated criterion using IRIS data.

Figure 3-1 shows the procedure for determining an updated criterion using IRIS data. If a chemical has both carcinogenic and non-carcinogenic effects, i.e., both a cancer potency estimate and a RfD, both criteria should be calculated. The most stringent criterion applies.

Calculating Criteria for Non-carcinogens

The RfD is an estimate of the daily exposure to the human population that is likely to be without appreciable risk of causing deleterious effects during a lifetime. The RfD is expressed in units of mg toxicant per kg human body weight per day.

RfDs are derived from the "no-observed-adverse-effect level" (NOAEL) or the "lowest-observed-adverse-effect level" (LOAEL) identified from chronic or subchronic human epidemiology studies or animal exposure studies. (Note: "LOAEL" and "NOAEL" refer to animal and human toxicology and are therefore distinct from the aquatic toxicity terms "no-observed-effect concentration" (NOEC) and "lowest-observed-effect concentration" (LOEC).) Uncertainty factors are then applied to the NOAEL or LOAEL to account for uncertainties in the data associated with variability among individuals, extrapolation from nonhuman test species to humans, data on other than long-term exposures, and the use of a LOAEL (USEPA, 1988a). An additional uncertainty factor may be applied to account for significant weakness or gaps in the database.

The RfD is a threshold below which systemic toxic effects are unlikely to occur. While exposures above the RfD increase the probability of adverse effects, they do not produce a certainty of adverse effects. Similarly, while exposure at or below the RfD reduces the probability, it does not guarantee the absence of effects in all persons. The RfDs contained in IRIS are values that represent EPA's consensus (and have uncertainty spanning perhaps an order of magnitude). This means an RfD of 1.0 mg/kg/day could range from 0.3 to 3.0 mg/kg/day.

For noncarcinogenic effects, an updated criterion can be derived using the equation in Exhibit 3-1.

If the receiving water body is not used as a drinking water source, the factor WI can be deleted. Where dietary and/or inhalation exposure values are unknown, these factors may be deleted from the above calculation.

Calculating Criteria for Carcinogens

Any human health criterion for a carcinogen is based on at least three interrelated considerations: cancer potency, exposure, and risk characterization. When developing State criteria, States may make their own judgments on each of these factors within reasonable scientific bounds, but documentation to support their judgments must be clear and in the public record.

Maximum protection of human health from the potential effects of exposure to carcinogens through the consumption of contaminated fish and/or other aquatic life would require a criterion of zero. The zero level is based upon the assumption of non-threshold effects (i.e., no safe level exists below which any increase in exposure does not result in an increased risk of cancer) for carcinogens. However, because a publicly acceptable policy for safety does not require the absence of all risk, a numerical estimate of pollutant concentration (in μg/l) which corresponds to a given level of risk for a population of a specified size is selected instead. A cancer risk level is defined as the number of new cancers that may result in a population of specified size due to an increase in exposure (e.g., 10^{-6} risk level = 1 additional cancer in a population of 1 million). Cancer risk is calculated by multiplying the experimentally derived cancer potency estimate by the concentration of the chemical in the fish and the average daily human consumption of contaminated fish. The risk for a specified population (e.g., 1 million people or 10^{-6}) is then calculated by dividing the risk level by the specific cancer risk. EPA's ambient water quality criteria documents provide risk levels ranging from 10^{-5} to 10^{-7} as examples.

The cancer potency estimate, or slope factor (formerly known as the q_1*), is derived using animal studies. High-dose exposures are extrapolated to low-dose concentrations and adjusted to a lifetime exposure period through the use of a linearized multistage model. The model calculates the upper 95 percent confidence limit of the slope of a straight line which the model postulates to occur at low doses. When based on human (epidemiological) data, the slope factor is based on the observed increase in cancer risk and is not extrapolated. For deriving criteria for carcinogens, the oral cancer potency estimates or slope factors from IRIS are used.

It is important to note that cancer potency factors may overestimate or underestimate the actual risk. Such potency estimates are subject to great uncertainty because of two primary factors:

$$C\ (mg/l) = \frac{(RfD \times WT) - (DT + IN) \times WT}{WI + [FC \times L \times FM \times BCF]}$$

where:

C	=	updated water quality criterion (mg/l)
RfD	=	oral reference dose (mg toxicant/kg human body weight/day)
WT	=	weight of an average human adult (70 kg)
DT	=	dietary exposure (other than fish) (mg toxicant/kg body human weight/day)
IN	=	inhalation exposure (mg toxicant/kg body human weight/day)
WI	=	average human adult water intake (2 l/day)
FC	=	daily fish consumption (kg fish/day)
L	=	ratio of lipid fraction of fish tissue consumed to 3%
FM	=	food chain multiplier (from Table 3-1)
BCF	=	bioconcentration factor (mg toxicant/kg fish divided by mg toxicant/L water) for fish with 3% lipid content

Exhibit 3-1. Equation for Deriving Human Health Criteria Based on Noncarcinogenic Effects

- adequacy of the cancer data base (i.e., human vs. animal data); and
- limited information regarding the mechanism of cancer causation.

Risk levels of 10^{-5}, 10^{-6}, and 10^{-7} are often used by States as minimal risk levels in interpreting their standards. EPA considers risks to be additive, i.e., the risk from individual chemicals is not necessarily the overall risk from exposure to water. For example, an individual risk level of 10^{-6} may yield a higher overall risk level if multiple carcinogenic chemicals are present.

For carcinogenic effects, the criterion can be determined by using the equation in Exhibit 3-2. If the receiving water body is not designated as a drinking water source, the factor WI can be deleted.

Deriving Quantitative Risk Assessments in the Absence of IRIS Values

The RfDs or cancer potency estimates comprise the existing dose-response factors for developing criteria. When IRIS data are unavailable, quantitative risk level information may be developed according to a State's own procedures. Some States have established their own procedures whereby dose-response factors can be developed based upon extrapolation of acute and/or chronic animal data to concentrations of exposure protective of fish consumption by

$$C\ (mg/l) = \frac{(RL \times WT)}{q_1^* \left[WI + FC \times L \times (FM \times BCF)\right]}$$

where:

C	=	updated water quality criterion (mg/l)
RL	=	risk level (10^{-x}) where x is usually in the range of 4 to 6
WT	=	weight of an average human adult (70 kg)
q_1^*	=	carcinogenic potency factor (kg day/mg)
WI	=	average human adult water intake (2 l/day)
FC	=	daily fish consumption (kg fish/day)
L	=	ratio of lipid fraction of fish tissue consumed to 3% assumed by EPA
FM	=	food chain multiplier (from Table 3-1)
BCF	=	bioconcentration factor (mg toxicant/kg fish divided by mg toxicant/L water) for fish with 3% lipid content

Exhibit 3-2. Equation for Deriving Human Health Criteria Based on Carcinogenic Effects

humans.

3.2 Relationship of Section 304(a) Criteria to State Designated Uses

The section 304(a)(1) criteria published by EPA from time to time can be used to support the designated uses found in State standards. The following sections briefly discuss the relationship between certain criteria and individual use classifications. Additional information on this subject also can be found in the "Green Book" (FWPCA, 1968); the "Blue Book" (NAS/NAE, 1973); the "Red Book" USEPA, 1976); the EPA *Water Quality Criteria Documents* (see Appendix I); the"Gold Book" (USEPA, 1986a); and future EPA section 304(a)(1) water quality criteria publications.

Where a water body is designated for more than one use, criteria necessary to protect the most sensitive use must be applied. The following four sections discuss the major types of use categories.

3.2.1 Recreation

Recreational uses of water include activities such as swimming, wading, boating, and fishing. Often insufficient data exist on the human health effects of physical and chemical pollutants, including most toxics, to make a determination of criteria for recreational uses. However, as a general guideline, recreational waters that contain chemicals in concentrations toxic or otherwise harmful to man if ingested, or irritating to the skin or mucous membranes of the human body upon brief immersion, should be avoided. The section 304(a)(1) human health effects criteria based on direct human drinking water intake and fish consumption might provide useful guidance in these circumstances. Also, section 304(a)(1) criteria based on human health effects may be used to support this designated use where fishing is included in the State definition of "recreation." In this latter situation, only the portion of the criterion based on fish consumption should be used. Section 304(a)(1) criteria to protect recreational uses are also available for certain physical, microbiological, and narrative "free from" aesthetic criteria.

Research regarding bacteriological indicators has resulted in EPA recommending that States use *Escherichia coli* or enterococci as indicators of recreational water quality (USEPA, 1986b) rather than fecal coliform because of the better correlation with gastroenteritis in swimmers.

The "Green Book" and "Blue Book" provide additional information on protecting recreational uses such as pH criteria to prevent eye irritation and microbiological criteria based on aesthetic considerations.

3.2.2 Aquatic Life

The section 304(a)(1) criteria for aquatic life should be used directly to support this designated use. If subcategories of this use are adopted (e.g., to differentiate between coldwater and warmwater fisheries), then appropriate criteria should be set to reflect the varying needs of such subcategories.

3.2.3 Agricultural and Industrial Uses

The "Green Book" (FWPCA, 1968) and "Blue Book" (NAS/NAE, 1973) provide some information on protecting agricultural and industrial uses. Section 304(a)(1) criteria for protecting these uses have not been specifically developed for numerous parameters pertaining to these uses, including most toxics. Where criteria have not been specifically developed for these uses, the criteria developed for human health and aquatic life are usually sufficiently stringent to protect these uses. States may also establish criteria specifically designed to protect these uses.

3.2.4 Public Water Supply

The drinking water exposure component of the section 304(a)(1) criteria based on human health effects can apply directly to this use classification. The criteria also may be appropriately modified depending upon whether the specific water supply system falls within the auspices of the Safe Drinking Water Act's (SDWA) regulatory control and the type and level of treatment imposed upon the supply before delivery to the consumer. The SDWA controls the presence of contaminants in finished ("at-the-tap") drinking water.

A brief description of relevant sections of the SDWA is necessary to explain how the Act will work in conjunction with section 304(a)(1) criteria in protecting human health from the effects of toxics due to consumption of water. Pursuant to section 1412 of the SDWA, EPA has promulgated "National Primary Drinking Water Standards" for certain radionuclide, microbiological, organic, and inorganic substances. These standards establish maximum contaminant levels (MCLs), which specify the maximum permissible level of a contaminant in water that may be delivered to a user of a public water system now defined as serving a minimum of 25 people. MCLs are established based on consideration of a range of factors including not only the health effects of the contaminants but also treatment capability, monitoring availability, and costs. Under section 1401(1)(D)(i) of the SDWA, EPA is also allowed to establish the minimum quality criteria for water that may be taken into a public water supply system.

Section 304(a)(1) criteria provide estimates of pollutant concentrations protective of human health, but do not consider treatment technology, costs, and other feasibility factors. The section

304(a)(1) criteria also include fish bioaccumulation and consumption factors in addition to direct human drinking water intake. These numbers were not developed to serve as "at-the-tap" drinking water standards, and they have no regulatory significance under the SDWA. Drinking water standards are established based on considerations, including technological and economic feasibility, not relevant to section 304(a)(1) criteria. Section 304(a)(1) criteria are more analogous to the maximum contaminant level goals (MCLGs) (previously known as RMCLs) under section 1412(b)(1)(B) of the SDWA in which, based upon a report from the National Academy of Sciences, the Administrator should set target levels for contaminants in drinking water at which "no known or anticipated adverse effects occur and which allow an adequate margin of safety." MCLGs do not take treatment, cost, and other feasibility factors into consideration. Section 304(a)(1) criteria are, in concept, related to the health-based goals specified in the MCLGs.

MCLs of the SDWA, where they exist, control toxic chemicals in finished drinking water. However, because of variations in treatment, ambient water criteria may be used by the States as a supplement to SDWA regulations. When setting water quality criteria for public water supplies, States have the option of applying MCLs, section 304(a)(1) human health effects criteria, modified section 304(a)(1) criteria, or controls more stringent than these three to protect against the effects of contaminants by ingestion from drinking water.

For treated drinking water supplies serving 25 people or greater, States must control contaminants down to levels at least as stringent as MCLs (where they exist for the pollutants of concern) in the finished drinking water. However, States also have the options to control toxics in the ambient water by choosing section 304(a)(1) criteria, adjusted section 304(a)(1) criteria resulting from the reduction of the direct drinking water exposure component in the criteria calculation to the extent that the treatment process reduces the level of pollutants, or a more stringent contaminant level than the former three options.

3.3 State Criteria Requirements

Section 131.11(a)(1) of the Regulation requires States to adopt water quality criteria to protect the designated use(s). The State criteria must be based on sound scientific rationale and must contain sufficient parameters or constituents to protect the designated use(s). For waters with multiple use designations, the criteria must support the most sensitive use.

In section 131.11, States are encouraged to adopt both numeric and narrative criteria. Aquatic life criteria should protect against both short-term (acute) and long-term (chronic) effects. Numeric criteria are particularly important where the cause of toxicity is known or for protection against pollutants with potential human health impacts or bioaccumulation potential. Numeric water quality criteria may also be the best way to address nonpoint source pollution problems. Narrative criteria can be the basis for limiting toxicity in waste discharges where a specific pollutant can be identified as causing or contributing to the toxicity but where there are no numeric criteria in the State standards. Narrative criteria also can be used where toxicity cannot be traced to a particular pollutant.

Section 131.11(a)(2) requires States to develop implementation procedures which explain how the State will ensure that narrative toxics criteria are met.

To more fully protect aquatic habitats, it is EPA's policy that States fully integrate chemical-specific, whole-effluent, and biological assessment approaches in State water quality programs (see Appendix R). Specifically, each of these three methods can provide a valid assessment of <u>non-attainment</u> of designated aquatic life uses but can rarely demonstrate use <u>attainment</u> separately. Therefore, EPA supports a policy of independent application of these three water quality assessment approaches. Independent application means that the validity of the results of any one of the approaches does not depend on confirmation by one or both of the other methods. This policy is based on the unique attributes, limitations, and program applications of each of the three approaches. Each method alone can provide valid and independently sufficient evidence of non-attainment of water quality standards, irrespective of any evidence, or lack thereof, derived from the other two approaches. The failure of one method to confirm impacts identified by another method does not negate the results of the initial assessment.

It is also EPA's policy that States should designate aquatic life uses that appropriately address biological integrity and adopt biological criteria necessary to protect those uses (see section 3.5.3 and Appendices C, K, and R).

3.4 Criteria for Toxicants

Applicable requirements for State adoption of water quality criteria for toxicants vary depending upon the toxicant. The reason for this is that the 1983 Water Quality Standards Regulation (Appendix A) and the Water Quality Act of 1987 which amended the Clean Water Act (Public Law 100-4) include more specific requirements for the particular toxicants listed pursuant to CWA section 307(a). For regulatory purposes, EPA has translated the 65 compounds and families of compounds listed pursuant to section 307(a) into 126 more specific substances, which EPA refers to as "priority toxic pollutants." The 126 priority toxic pollutants are listed in the WQS regulation and in Appendix P of this Handbook. Because of the more specific requirements for priority toxic pollutants, it is convenient to organize the requirements applicable to State adoption of criteria for toxicants into three categories:

- requirements applicable to priority toxic pollutants that have been the subject of CWA section 304(a)(1) criteria guidance (see section 3.4.1);
- requirements applicable to priority toxic pollutants that have not been the subject of CWA section 304(a)(1) criteria guidance (see section 3.4.1); and
- requirements applicable to all other toxicants (e.g., non-conventional pollutants like ammonia and chlorine) (see section 3.4.2).

3.4.1 Priority Toxic Pollutant Criteria

The criteria requirements applicable to priority toxic pollutants (i.e., the first two categories above) are specified in CWA section 303(c)(2)(B). Section 303(c)(2)(B), as added by the Water Quality Act of 1987, provides that:

> Whenever a State reviews water quality standards pursuant to paragraph (1) of this subsection, or revises or adopts new standards pursuant to this paragraph, such State shall adopt criteria for all toxic pollutants listed pursuant to section 307(a)(1) of this Act for which criteria have been published under section 304(a), the discharge or presence of which in the affected waters could reasonably be expected to interfere with those designated uses adopted by the State, as necessary to support such designated uses. Such criteria shall be specific numerical criteria for such toxic pollutants. Where such numerical criteria are not available, whenever a State reviews water quality standards pursuant to paragraph (1), or revises or adopts new standards pursuant to this paragraph, such State shall adopt criteria based on biological monitoring or assessment methods consistent with information published pursuant to section 304(a)(8). Nothing in this section shall be construed to limit or delay the use of effluent limitations or other permit conditions based on or involving biological monitoring or assessment

methods or previously adopted numerical criteria.

EPA, in devising guidance for section 303(c)(2)(B), attempted to provide States with the maximum flexibility that complied with the express statutory language but also with the overriding congressional objective: prompt adoption and implementation of numeric toxics criteria. EPA believed that flexibility was important so that each State could comply with section 303(c)(2)(B) and to the extent possible, accommodate its existing water quality standards regulatory approach.

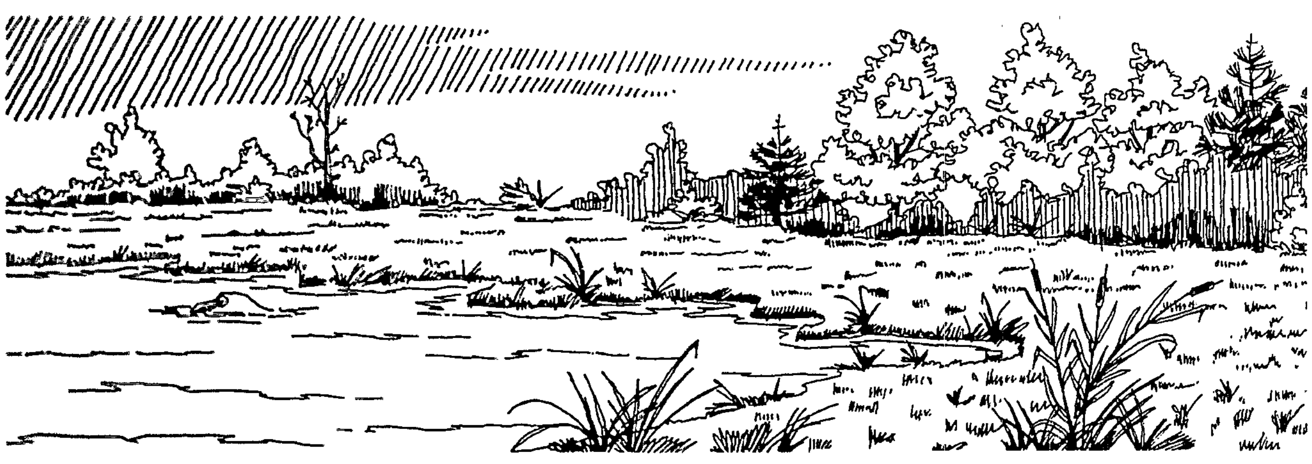
General Requirements

To carry out the requirements of section 303(c)(2)(B), whenever a State revises its water quality standards, it must review all available information and data to first determine whether the discharge or the presence of a toxic pollutant is interfering with or is likely to interfere with the attainment of the designated uses of any water body segment.

If the data indicate that it is reasonable to expect the toxic pollutant to interfere with the use, or it actually is interfering with the use, then the State must adopt a numeric limit for the specific pollutant. If a State is unsure whether a toxic pollutant is interfering with, or is likely to interfere with, the designated use and therefore is unsure that control of the pollutant is necessary to support the designated use, the State should undertake to develop sufficient information upon which to make such a determination. Presence of facilities that manufacture or use the section 307(a) toxic pollutants or other information indicating that such pollutants are discharged or will be discharged strongly suggests that such pollutants could be interfering with attaining designated uses. If a State expects the pollutant not to interfere with the designated use, then section 303(1)(2)(B) does not require a numeric standard for that pollutant.

Section 303(c)(2)(B) addresses only pollutants listed as "toxic" pursuant to section 307(a) of the Act, which are codified at 40 CFR 131.36(b). The section 307(a) list contains 65 compounds and families of compounds, which potentially include thousands of specific compounds. The Agency has interpreted that list to include 126 "priority" toxic pollutants for regulatory purposes. Reference in this guidance to toxic pollutants or section 307(a) toxic pollutants refers to the 126 priority toxic pollutants unless otherwise noted. Both the list of priority toxic pollutants and recommended criteria levels are subject to change.

The national criteria recommendations published by EPA under section 304(a) (see section 3.1, above) of the Act include values for both acute and chronic aquatic life protection; only chronic criteria recommendations have been established to



protect human health. To comply with the statute, a State needs to adopt aquatic life and human health criteria where necessary to support the appropriate designated uses. Criteria for the protection of human health are needed for water bodies designated for public water supply. When fish ingestion is considered an important activity, then the human health-related water quality criteria recommendation developed under section 304(a) of the CWA should be used; that is, the portion of the criteria recommendation based on fish consumption. For those pollutants designated as carcinogens, the recommendation for a human health criterion is generally more stringent than the aquatic life criterion for the same pollutant. In contrast, the aquatic life criteria recommendations for noncarcinogens are generally more stringent than the human health recommendations. When a State adopts a human health criterion for a carcinogen, the State needs to select a risk level. EPA has estimated risk levels of 10^{-5}, 10^{-6}, and 10^{-7} in its criteria documents under one set of exposure assumptions. However, the State is not limited to choosing among the risk levels published in the section 304(a) criteria documents, nor is the State limited to the base case exposure assumptions; it must choose the risk level for its conditions and explain its rationale.

EPA generally regulates pollutants treated as carcinogens in the range of 10^{-6} to 10^{-4} to protect average exposed individuals and more highly exposed populations. However, if a State selects a criterion that represents an upper bound risk level less protective than 1 in 100,000 (e.g., 10^{-5}), the State needs to have substantial support in the record for this level. This support focuses on two distinct issues. First, the record must include documentation that the decision maker considered the public interest of the State in selecting the risk level, including documentation of public participation in the decision making process as required by the Water Quality Standards Regulation at 40 CFR 131.20(b). Second, the record must include an analysis showing that the risk level selected, when combined with other risk assessment variables, is a balanced and reasonable estimate of actual risk posed, based on the best and most representative information available. The importance of the estimated actual risk increases as the degree of conservatism in the selected risk level diminishes. EPA carefully evaluates all assumptions used by a State if the State chose to alter any one of the standard EPA assumption values (57 F.R. 60864, December 22, 1993).

EPA does not intend to propose changes to the current requirements regarding the bases on which a State can adopt numeric criteria (40 CFR 131.11(b)(1)). Under EPA's regulation, in addition to basing numeric criteria on EPA's section 304(a) criteria documents, States may also base numeric criteria on site-specific determinations or other scientifically defensible methods.

EPA expects each State to comply with the new statutory requirements in any section 303(c) water quality standards review initiated after enactment of the Water Quality Act of 1987. The structure of section 303(c) is to require States to review their water quality standards at least once each 3 year period. Section 303(c)(2)(B) instructs States to include reviews for toxics criteria whenever they initiate a triennial review. Therefore, even if a State has complied with section 303(c)(2)(B), the State must review its standards each triennium to ensure that section 303(c)(2)(B) requirements continue to be met, considering that EPA may have published additional section 304(a) criteria documents and that the State will have new information on existing water quality and on pollution sources.

It should be noted that nothing in the Act or in the Water Quality Standards Regulation restricts the right of a State to adopt numeric criteria for any pollutant not listed pursuant to section 307(a)(1), and that such criteria may be expressed as concentration limits for an individual pollutant or for a toxicity parameter itself as measured by whole-effluent toxicity testing. However, neither numeric toxic criteria nor whole-effluent toxicity should be used as a surrogate for, or to supersede the other.

State Options

States may meet the requirements of CWA section 303(c)(2)(B) by choosing one of three scientifically and technically sound options (or some combination thereof):

(1) Adopt statewide numeric criteria in State water quality standards for all section 307(a) toxic pollutants for which EPA has developed criteria guidance, regardless of whether the pollutants are known to be present;

(2) Adopt specific numeric criteria in State water quality standards for section 307(a) toxic pollutants as necessary to support designated uses where such pollutants are discharged or are present in the affected waters and could reasonably be expected to interfere with designated uses;

(3) Adopt a "translator procedure" to be applied to a narrative water quality standard provision that prohibits toxicity in receiving waters. Such a procedure is to be used by the State in calculating derived numeric criteria, which shall be used for all purposes under section 303(c) of the CWA. At a minimum, such criteria need to be developed for section 307(a) toxic pollutants, as necessary to support designated uses, where these pollutants are discharged or present in the affected waters and could reasonably be expected to interfere with designated uses.

Option 1 is consistent with State authority to establish water quality standards. Option 2 most directly reflects the CWA requirements and is the option recommended by EPA. Option 3, while meeting the requirements of the CWA, is best suited to supplement numeric criteria from option 1 or 2. The three options are discussed in more detail below.

OPTION 1

Adopt statewide numeric criteria in State water quality standards for all section 307(a) toxic pollutants for which EPA has developed criteria guidance, regardless of whether the pollutants are known to be present.

Pro:

- simple, straightforward implementation
- ensures that States will satisfy statute
- makes maximum uses of EPA recommendations
- gets specific numbers into State water quality standards fast, at first

Con:

- some priority toxic pollutants may not be discharged in State
- may cause unnecessary monitoring by States
- might result in "paper standards"

Option 1 is within a State's legal authority under the CWA to adopt broad water quality standards. This option is the most comprehensive approach to satisfy the statutory requirements because it would include all of the priority toxic pollutants for which EPA has prepared section 304(a) criteria guidance for either or both aquatic life protection and human health protection. In addition to a simple adoption of EPA's section 304(a) guidance as standards, a State must select a risk level for those toxic pollutants which are carcinogens (i.e., that cause or may cause cancer in humans).

Many States find this option attractive because it ensures comprehensive coverage of the priority toxic pollutants with scientifically defensible criteria without the need to conduct a resource-intensive evaluation of the particular segments and pollutants requiring criteria. This option also would not be more costly to dischargers than other options because permit limits would be based only on the regulation of the particular toxic pollutants in their discharges and not on the total listing in the water quality standards. Thus, actual permit limits should be the same under any of the options.

The State may also exercise its authority to use one or more of the techniques for adjusting water quality standards:

- establish or revise designated stream uses based on use attainability analyses (see section 2.9);
- develop site-specific criteria; or
- allow short-term variances (see section 5.3) when appropriate.

All three of these techniques may apply to standards developed under any of the three options discussed in this guidance. It is likely that States electing to use option 1 will rely more on variances because the other two options are implemented with more site-specific data being available. It should be noted, however, that permits issued pursuant to such water quality variances still must comply with any applicable antidegradation and antibacksliding requirements.

OPTION 2

Adopt specific numeric criteria in State water quality standards for section 307(a) toxic pollutants as necessary to support designated uses where such pollutants are discharged or are present in the affected waters and could reasonably be expected to interfere with designated uses.

Pro:

- directly reflects statutory requirement
- standards based on demonstrated need to control problem pollutants
- State can use EPA's section 304(a) national criteria recommendations or other scientifically acceptable alternative, including site-specific criteria
- State can consider current or potential toxic pollutant problems
- State can go beyond section 307(a) toxics list, as desired

Con:

- may be difficult and time consuming to determine if, and which, pollutants are interfering with the designated use
- adoption of standards can require lengthy debates on correct criteria limit to be included in standards
- successful State toxic control programs based on narrative criteria may be halted or slowed as the State applies its limited resources to developing numeric standards
- difficult to update criteria once adopted as part of standards
- to be absolutely technically defensible, may need site-specific criteria in many situations, leading to a large workload for regulatory agency

EPA recommends that a State use this option to meet the statutory requirement. It directly reflects all the Act's requirements and is flexible, resulting in adoption of numeric water quality standards as needed. To assure that the State is capable of dealing with new problems as they arise, EPA also recommends that States adopt a translator procedure the same as, or similar to, that described in option 3, but applicable to all chemicals causing toxicity and not just priority pollutants as is the case for option 3.

Beginning in 1988, EPA provided States with candidate lists of priority toxic pollutants and water bodies in support of CWA section 304(l) implementation. These lists were developed because States were required to evaluate existing and readily available water-related data to comply with section 304(l), 40 CFR 130.10(d). A similar "strawman" analysis of priority pollutants potentially requiring adoption of numeric criteria under section 303(c)(2)(B) was furnished to most States in September or October of 1990 for their use in ongoing and subsequent triennial reviews. The primary differences between the "strawman" analysis and the section 304(l) candidate lists were that the "strawman" analysis (1) organized the results by chemical rather than by water body, (2) included data for certain STORET monitoring stations that were not used in constructing the candidate lists, (3) included data from the Toxics Release Inventory database, and (4) did not include a number of data sources used in preparing the candidate lists (e.g., those, such as fish kill information, that did not provide chemical-specific information).

EPA intends for States, at a minimum, to use the information gathered in support of section 304(l) requirements as a starting point for identifying (1) water segments that will need new and/or revised water quality standards for section 307(a) toxic pollutants, and (2) which priority toxic pollutants require adoption of numeric criteria. In the longer term, EPA expects similar determinations to occur during each triennial review of water quality standards as required by section 303(c).

In identifying the need for numeric criteria, EPA is encouraging States to use information and data such as:

- presence or potential construction of facilities that manufacture or use priority toxic pollutants;
- ambient water monitoring data, including those for sediment and aquatic life (e.g., fish tissue data);
- NPDES permit applications and permittee self-monitoring reports;
- effluent guideline development documents, many of which contain section 307(a)(1) priority pollutant scans;
- pesticide and herbicide application information and other records of pesticide or herbicide inventories;
- public water supply source monitoring data noting pollutants with Maximum Contaminant Levels (MCLs); and
- any other relevant information on toxic pollutants collected by Federal, State, interstate agencies, academic groups, or scientific organizations.

States are also expected to take into account newer information as it became available, such as information in annual reports from the Toxic Chemical Release Inventory requirements of the Emergency Planning and Community Right-To-Know Act of 1986 (Title III, Public Law 99-499).

Where the State's review indicates a reasonable expectation of a problem from the discharge or presence of toxic pollutants, the State should identify the pollutant(s) and the relevant segment(s). In making these determinations, States should use their own EPA-approved criteria or existing EPA water quality criteria for purposes of segment identification. After the review, the State may use other means to establish the final criterion as it revises its standards.

As with option 1, a State using option 2 must follow all its legal and administrative requirements for adoption of water quality standards. Since the resulting numeric criteria are part of a State's water quality standards, they are required to be submitted by the State to EPA for review and either approval or disapproval.

EPA believes this option offers the State optimum flexibility. For section 307(a) toxic pollutants adversely affecting designated uses, numeric criteria are available for permitting purposes. For other situations, the State has the option of defining site-specific criteria.

OPTION 3

Adopt a procedure to be applied to the narrative water quality standard provision that prohibits toxicity in receiving waters. Such a procedure would be used by a State in calculating derived numeric criteria to be used for all purposes of water quality criteria under section 303(c) of the CWA. At a minimum such criteria need to be derived for section 307(a) toxic pollutants where the discharge or presence of such pollutants in the affected waters could reasonably be expected to interfere with designated uses, as necessary to support such designated uses.

Pro:

- allows a State flexibility to control priority toxic pollutants
- reduces time and cost required to adopt specific numeric criteria as water quality standards regulations
- allows immediate use of latest scientific information available at the time a State needs to develop derived numeric criteria
- revisions and additions to derived numeric criteria can be made without need to revise State law
- State can deal more easily with a situation where it did not establish water quality standards for the section 307(a) toxic pollutants during the most recent triennial review
- State can address problems from non-section 307(a) toxic pollutants

Con:

- EPA is currently on notice that a derived numeric criterion may invite legal challenge
- once the necessary procedures are adopted to enhance legal defensibility (e.g., appropriate scientific methods and public participation and review), actual savings in time and costs may be less than expected
- public participation in development of derived numeric criteria may be limited when such criteria are not addressed in a hearing on water quality standards

EPA believes that adoption of a narrative standard along with a translator mechanism as part of a State's water quality standard satisfies the substantive requirements of the statute. These criteria are subject to all the State's legal and administrative requirements for adoption of standards plus review and either approval or disapproval by EPA, and result in the development of derived numeric criteria for specific section 307(a) toxic pollutants. They are also subject to an opportunity for public participation. Nevertheless, EPA believes the most appropriate use of option 3 is as a supplement to either option 1 or 2. Thus, a State would have formally adopted numeric criteria for toxic pollutants that occur frequently; that have general applicability statewide for inclusion in NPDES permits, total maximum daily loads, and waste load allocations; and that also would have a sound and predictable method to develop additional numeric criteria as needed. This combination of options provides a complete regulatory scheme.

Although the approach in option 3 is similar to that currently allowed in the Water Quality Standards Regulation (40 CFR 131.11(a)(2)), this guidance discusses several administrative and scientific requirements that EPA believes are necessary to comply with section 303(c)(2)(B).

(1) The Option 3 Procedure Must Be Used To Calculate Derived Numeric Water Quality Criteria

States must adopt a specific procedure to be applied to a narrative water quality criterion. To satisfy section 303(c)(2)(B), this procedure shall be used by the State in calculating derived numeric criteria, which shall be used for all purposes under section 303(c) of the CWA. Such criteria need to be developed for section 307(a) toxic pollutants as necessary to support designated uses, where these pollutants are discharged or are present in the affected waters and could reasonably be expected to interfere with the designated uses.

To assure protection from short-term exposures, the State procedure should ensure development of derived numeric water quality criteria based on valid acute aquatic toxicity tests that are lethal to half the affected organisms (LC50) for the species representative of or similar to those found in the State. In addition, the State procedure should ensure development of derived numeric water quality criteria for protection from chronic exposure by using an appropriate safety factor applicable to this acute limit. If there are saltwater components to the State's aquatic resources, the State should establish appropriate derived numeric criteria for saltwater in addition to those for freshwater.

The State's documentation of the tests should include a detailed discussion of its quality control and quality assurance procedures. The State should also include a description (or reference existing technical agreements with EPA) of the procedure it will use to calculate derived acute and chronic numeric criteria from the test data, and how these derived criteria will be used as the basis for deriving appropriate TMDLs, WLAs, and NPDES permit limits.

As discussed above, the procedure for calculating derived numeric criteria needs to protect aquatic life from both acute and chronic exposure to specific chemicals. Chronic aquatic life criteria are to be met at the edge of the mixing zone. The acute criteria are to be met (1) at the end-of-pipe if mixing is not rapid and complete and a high rate diffuser is not present; or (2) after mixing if mixing is rapid and complete or a high rate diffuser is present. (See EPA's *Technical Support Document for Water Quality-based Toxics Control*, USEPA 1991a.)

EPA has not established a national policy specifying the point of application in the receiving water to be used with human health criteria. However, EPA has approved State standards that apply human health criteria for fish consumption at the mixing zone boundary and/or apply the criteria for drinking water consumption, at a minimum, at the point of use. EPA has also <u>proposed</u> more stringent requirements for the application of human health criteria for highly bioaccumulative pollutants in the *Water Quality guidance for the Great Lakes System* (50 F.R. 20931, 21035, April 16, 1993) including elimination of mixing zones.

In addition, the State should also include an indication of potential bioconcentration or bioaccumulation by providing for:

- laboratory tests that measure the steady-state bioconcentration rate achieved by a susceptible organism; and/or

- field data in which ambient concentrations and tissue loads are measured to give an appropriate factor.

In developing a procedure to be used in calculating derived numeric criteria for the protection of aquatic life, the State should consider the potential impact that bioconcentration has on aquatic and terrestrial food chains.

The State should also use the derived bioconcentration factor and food chain multiplier to calculate chronically protective numeric criteria for humans that consume aquatic organisms. In calculating this derived numeric criterion, the State should indicate data requirements to be met when dealing with either threshold (toxic) or non-threshold (carcinogenic) compounds. The State should describe the species and the minimum number of tests, which may generally be met by a single mammalian chronic test if it is of good quality and if the weight of evidence indicates that the results are reasonable. The State should provide the method to calculate a derived numeric criterion from the appropriate test result.

Both the threshold and non-threshold criteria for protecting human health should contain exposure assumptions, and the State procedure should be used to calculate derived numeric criteria that address the consumption of water, consumption of fish, and combined consumption of both water and fish. The State should provide the assumptions regarding the amount of fish and the quantity of water consumed per person per day, as well as the rationale used to select the assumptions. It needs to include the number of tests, the species necessary to establish a dose-response relationship, and the procedure to be used to calculate the derived numeric criteria. For non-threshold contaminants, the State should specify the model used to extrapolate to low dose and the risk level. It should also address incidental exposure from other water sources (e.g., swimming). When calculating derived numeric criteria for multiple exposure to pollutants, the State should consider additive effects, especially for carcinogenic substances, and should factor in the contribution to the daily intake of toxicants from other sources (e.g., food, air) when data are available.

(2) The State Must Demonstrate That the Procedure Results in Derived Numeric Criteria Are Protective

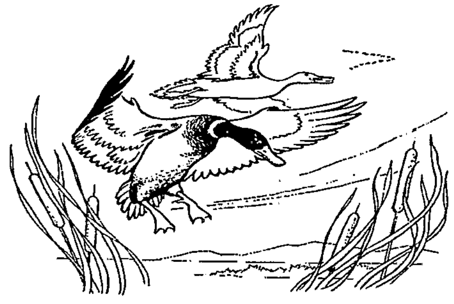
The State needs to demonstrate that its procedures for developing criteria, including translator methods, yield fully protective criteria for human health and for aquatic life. EPA's review process will proceed according to EPA's regulation of 40 CFR 131.11, which requires that criteria be based on sound scientific rationale and be protective of all designated uses. EPA will use the expertise and experience it has gained in developing section 304(a) criteria for toxic pollutants by application of its own translator method (USEPA, 1980b; USEPA, 1985b).

Once EPA has approved the State's procedure, the Agency's review of derived numeric criteria, for example, for pollutants other than section 307(a) toxic pollutants resulting from the State's procedure, will focus on the adequacy of the data base rather than the calculation method. EPA also encourages States to apply such a procedure to calculate derived numeric criteria to be used as the basis for deriving permit limitations for nonconventional pollutants that also cause toxicity.

(3) The State Must Provide Full Opportunity for Public Participation in Adoption of the Procedure

The Water Quality Standards Regulation requires States to hold public hearings to review and revise water quality standards in accordance with provisions of State law and EPA's Public Participation Regulation (40 CFR 25). Where a State plans to adopt a procedure to be applied to the narrative criterion, it must provide full opportunity for public participation in the development and adoption of the procedure as part of the State's water quality standards.

While it is not necessary for the State to adopt each derived numeric criterion into its water quality standards and submit it to EPA for review and approval, EPA is very concerned that all affected parties have adequate opportunity to participate in the development of a derived



numeric criterion even though it is not being adopted directly as a water quality standard.

A State can satisfy the need to provide an opportunity for public participation in the development of derived numeric criteria in several ways, including:

- a specific hearing on the derived numeric criterion;
- the opportunity for a public hearing on an NPDES permits as long as public notice is given that a criterion for a toxic pollutant as part of the permit issuance is being contemplated; or
- a hearing coincidental with any other hearing as long as it is made clear that development of a specific criterion is also being undertaken.

For example, as States develop their lists and individual control strategies (ICSs) under section 304(1), they may seek full public participation. NPDES regulations also specify public participation requirements related to State permit issuance. Finally, States have public participation requirements associated with Water Quality Management Plan updates. States may take advantage of any of these public participation requirements to fulfill the requirement for public review of any resulting derived numeric criteria. In such cases, the State must give prior notice that development of such criteria is under consideration.

(4) The Procedure Must Be Formally Adopted and Mandatory

Where a State elects to supplement its narrative criterion with an accompanying implementing procedure, it must formally adopt such a procedure as a part of its water quality standards. The procedure must be used by the State to calculate derived numeric criteria that will be used as the basis for all standards' purposes, including the following: developing TMDLs, WLAs, and limits in NPDES permits; determining whether water use designations are being met; and identifying potential nonpoint source pollution problems.

(5) The Procedure Must Be Approved by EPA as Part of the State's Water Quality Standards Regulation

To be consistent with the requirements of the Act, the State's procedure to be applied to the narrative criterion must be submitted to EPA for review and approval, and will become a part of the State's water quality standards. (See 40 CFR 131.21 for further discussion.) This requirement may be satisfied by a reference in the standards to the procedure, which may be contained in another document, which has legal effect and is binding on the State, and all the requirements for public review, State implementation, and EPA review and approval are satisfied.

Criteria Based on Biological Monitoring

For priority toxic pollutants for which EPA has not issued section 304(a)(1) criteria guidance, CWA section 303(c)(2)(B) requires States to adopt criteria based on biological monitoring or assessment methods. The phrase "biological monitoring or assessment methods" includes:

- whole-effluent toxicity control methods;
- biological criteria methods; or
- other methods based on biological monitoring or assessment.

The phrase "biological monitoring or assessment methods" in its broadest sense also includes criteria developed through translator procedures. This broad interpretation of that phrase is consistent with EPA's policy of applying chemical-specific, biological, and whole-effluent toxicity methods independently in an integrated toxics control program. It is also consistent with the intent of Congress to expand State standards programs beyond chemical-specific approaches.

States should also consider developing protocols to derive and adopt numeric criteria for priority toxic pollutants (or other pollutants) where EPA has not issued section 304(a) criteria guidance. The State should consider available laboratory toxicity test data that may be sufficient to support derivation of chemical-specific criteria. Existing data need not be as comprehensive as that required to meet EPA's 1985 guidelines in order for a State to use its own protocols to derive criteria. EPA has described such protocols in the proposed *Water Quality Guidance for the Great Lakes System* (58 F.R. 20892, at 21016, April 16, 1993.) This is particularly important where other components of a State's narrative criterion implementation procedure (e.g., WET controls or biological criteria) may not ensure full protection of designated uses. For some pollutants, a combination of chemical-specific and other approaches is necessary (e.g., pollutants where bioaccumulation in fish tissue or water consumption by humans is a primary concern).

Biologically based monitoring or assessment methods serve as the basis for control where no specific numeric criteria exist or where calculation or application of pollutant-by-pollutant criteria appears infeasible. Also, these methods may serve as a supplemental measurement of attainment of water quality standards in addition to numeric and narrative criteria. The requirement for both numeric criteria and biologically based methods demonstrates that section 303(c)(2)(B) contemplates that States develop a comprehensive toxics control program regardless of the status of EPA's section 304(a) criteria.

The whole-effluent toxicity (WET) testing procedure is the principal biological monitoring guidance developed by EPA to date. The purpose of the WET procedure is to control point source dischargers of toxic pollutants. The procedure is particularly useful for monitoring and controlling the toxicity of complex effluents that may not be well controlled through chemical-specific numeric criteria. As such, biologically based effluent testing procedures are a necessary component of a State's toxics control program under section 303(c)(2)(B) and a principal means for implementing a State's narrative "free from toxics" standard.

Guidance documents EPA considers to serve the purpose of section 304(a)(8) include the *Technical Support Document for Water Quality-based Toxics Control* (USEPA, 1991a; *Guidelines for Deriving National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses* (Appendix H); *Guidelines and Methodology Used in the Preparation of Health Effect Assessment Chapters of the Consent Decree Water Criteria Documents* (Appendix J); *Methods for Measuring Acute Toxicity of Effluents to Freshwater and Marine Organisms* (USEPA, 1991d); *Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms* (USEPA, 1991e); and *Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms* (USEPA, 1991f).

3.4.2 Criteria for Nonconventional Pollutants

Criteria requirements applicable to toxicants that are not priority toxic pollutants (e.g., ammonia and chlorine), are specified in the 1983 Water Quality Standards Regulation (see 40 CFR 131.11). Under these requirements, States must adopt criteria based on sound scientific rationale that cover sufficient parameters to protect designated uses. Both numeric and narrative criteria (discussed in sections 3.5.1 and 3.5.2, below) may be applied to meet these requirements.

3.5 Forms of Criteria

States are required to adopt water quality criteria, based on sound scientific rationale, that contain sufficient parameters or constituents to protect the designated use. EPA believes that an effective State water quality standards program should include both parameter-specific (e.g., ambient numeric criteria) and narrative approaches.

3.5.1 Numeric Criteria

Numeric criteria are required where necessary to protect designated uses. Numeric criteria to protect aquatic life should be developed to address both short-term (acute) and long-term (chronic) effects. Saltwater species, as well as freshwater species, must be adequately protected. Adoption of numeric criteria is particularly important for toxicants known to be impairing surface waters and for toxicants with potential human health impacts (e.g., those with high bioaccumulation potential). Human health should be protected from exposure resulting from consumption of water and fish or other aquatic life (e.g., mussels, crayfish). Numeric water quality criteria also are useful in addressing nonpoint source pollution problems.

In evaluating whether chemical-specific numeric criteria for toxicants that are <u>not</u> priority toxic pollutants are required, States should consider whether other approaches (such as whole-effluent toxicity criteria or biological controls) will ensure full protection of designated uses. As mentioned above, a combination of independent approaches may be required in some cases to support the designated uses and comply with the requirements of the Water Quality Standards Regulation (e.g., pollutants where bioaccumulation in fish tissue or water consumption by humans is a primary concern).

3.5.2 Narrative Criteria

To supplement numeric criteria for toxicants, all States have also adopted narrative criteria for toxicants. Such narrative criteria are statements that describe the desired water quality goal, such as the following:

> All waters, including those within mixing zones, shall be free from substances attributable to wastewater discharges or other pollutant sources that:
>
> (1) Settle to form objectional deposits;
>
> (2) Float as debris, scum, oil, or other matter forming nuisances;
>
> (3) Produce objectionable color, odor, taste, or turbidity;
>
> (4) Cause injury to, or are toxic to, or produce adverse physiological responses in humans, animals, or plants; or
>
> (5) Produce undesirable or nuisance aquatic life (54 F.R. 28627, July 6, 1989).

EPA considers that the narrative criteria apply to all designated uses at all flows and are necessary to meet the statutory requirements of section 303(c)(2)(A) of the CWA.

Narrative toxic criteria (No. 4, above) can be the basis for establishing chemical-specific limits for waste discharges where a specific pollutant can be identified as causing or contributing to the toxicity and the State has not adopted chemical-specific numeric criteria. Narrative toxic criteria are cited as a basis for establishing whole-effluent toxicity controls in EPA permitting regulations at 40 CFR 122.44(d)(1)(v).

To ensure that narrative criteria for toxicants are attained, the Water Quality Standards Regulation requires States to develop implementation procedures (see 40 CFR 131.11(a)(2)). Such implementation procedures (Exhibit 3-3) should address all mechanisms to be used by the State to ensure that narrative criteria are attained. Because implementation of chemical-specific numeric criteria is a key component of State toxics control programs, narrative criteria implementation procedures must describe or reference the State's procedures to implement such chemical-specific numeric criteria (e.g., procedures for establishing chemical-specific permit limits under the NPDES permitting

State implementation procedures for narrative toxics criteria should describe the following:

- Specific, scientifically defensible methods by which the State will implement its narrative toxics standard for all toxicants, including:

  - methods for chemical-specific criteria, including methods for applying chemical-specific criteria in permits, developing or modifying chemical-specific criteria via a "translator procedure" (defined and discussed below), and calculating site-specific criteria based on local water chemistry or biology);

  - methods for developing and implementing whole-effluent toxicity criteria and/or controls; and

  - methods for developing and implementing biological criteria.

- How these methods will be integrated in the State's toxics control program (i.e., how the State will proceed when the specified methods produce conflicting or inconsistent results).

- Application criteria and information needed to apply numerical criteria, for example:

  - methods the State will use to identify those pollutants to be regulated in a specific discharge;

  - an incremental cancer risk level for carcinogens;

  - methods for identifying compliance thresholds in permits where calculated limits are below detection;

  - methods for selecting appropriate hardness, pH, and temperature variables for criteria expressed as functions;

  - methods or policies controlling the size and in-zone quality of mixing zones;

  - design flows to be used in translating chemical-specific numeric criteria for aquatic life and human health into permit limits; and

  - other methods and information needed to apply standards on a case-by-case basis.

Exhibit 3-3. Components of a State Implementation Procedure for Narrative Toxics Criteria

program). Implementation procedures must also address State programs to control whole-effluent toxicity (WET) and may address programs to implement biological criteria, where such programs have been developed by the State. Implementation procedures therefore serve as umbrella documents that describe how the State's various toxics control programs are integrated to ensure adequate protection for aquatic life and human health and attainment of the narrative toxics criterion. In essence, the procedure should apply the "independent application" principle, which provides for independent evaluations of attainment of a designated use based on chemical-specific, whole-effluent toxicity, and biological criteria methods (see section 3.5.3 and Appendices C, K, and R).

EPA encourages, and may ultimately require, State implementation procedures to provide for implementation of biological criteria. However, the regulatory basis for requiring whole-effluent toxicity (WET) controls is clear. EPA regulations at 40 CFR 122.44(d)(1)(v) require NPDES permits to contain WET limits where a permittee has been shown to cause, have the reasonable potential to cause, or contribute to an in-stream excursion of a narrative criterion. Implementation of chemical-specific controls is also required by EPA regulations at 40 CFR 122.44(d)(1). State implementation procedures should, at a minimum, specify or reference methods to be used in implementing chemical-specific and whole-effluent toxicity-based controls, explain how these methods are integrated, and specify needed application criteria.

In addition to EPA's regulation at 40 CFR 131, EPA has regulations at 40 CFR 122.44 that cover the National Surface Water Toxics Control Program. These regulations are intrinsically linked to the requirements to achieve water quality standards, and specifically address the control of pollutants both with and without numeric criteria. For example, section 122.44(d)(1)(vi) provides the permitting authority with several options for establishing effluent limits when a State does not have a chemical-specific numeric criterion for a pollutant present in an effluent at a concentration that causes or contributes to a violation of the State's narrative criteria.

3.5.3 Biological Criteria

The Clean Water Act of 1972 directs EPA to develop programs that will evaluate, restore, and maintain the chemical, physical, and biological integrity of the Nation's waters. In response to this directive, States and EPA have implemented chemically based water quality programs that address significant water pollution problems. However, over the past 20 years, it has become apparent that these programs alone cannot identify and address all surface water pollution problems. To help create a more comprehensive program, EPA is setting a priority for the development of biological criteria as part of State water quality standards. This effort will help States and EPA (1) achieve the biological integrity objective of the CWA set forth in section 101, and (2) comply with the statutory requirements under sections 303 and 304 of the Act (see Appendices C and K).

Regulatory Bases for Biocriteria

The primary statutory basis for EPA's policy that States should develop biocriteria is found in sections 101(a) and 303(c)(2)(B) of the Clean Water Act. Section 101(a) of the CWA gives the general goal of biological criteria. It establishes as the objective of the Act the restoration and maintenance of the chemical, physical, and biological integrity of the Nation's waters. To meet this objective, water quality criteria should address biological integrity. Section 101(a) includes the interim water quality goal for the protection and propagation of fish, shellfish, and wildlife.

Section 304(a) of the Act provides the legal basis for the development of informational criteria, including biological criteria. Specific directives for the development of regulatory biocriteria can be found in section 303(c), which requires EPA to develop criteria based on biological assessment methods when numerical criteria are not established.

Section 304(a) directs EPA to develop and publish water quality criteria and information on methods for measuring water quality and establishing water quality criteria for toxic pollutants on bases other than pollutant-by-pollutant, including biological monitoring and assessment methods that assess:

- the effects of pollutants on aquatic community components (". . . plankton, fish, shellfish, wildlife, plant life . . .") and community attributes (". . . biological community diversity, productivity, and stability . . .") in any body of water; and

- factors necessary " . . . to restore and maintain the chemical, physical, and biological integrity of all navigable waters . . ." for " . . . the protection of shellfish, fish, and wildlife for classes and categories of receiving waters . . . ."

Once biocriteria are formally adopted into State standards, biocriteria and aquatic life use designations serve as direct, legal endpoints for determining aquatic life use attainment/non-attainment. CWA section 303(c)(2)(B) provides that when numeric criteria are not available, States shall adopt criteria for toxics based on biological monitoring or assessment methods; biocriteria can be used to meet this requirement.

Development and Implementation of Biocriteria

Biocriteria are numerical values or narrative expressions that describe the expected reference biological integrity of aquatic communities inhabiting waters of a designated aquatic life use. In the most desirable scenario, these would be waters that are either in pristine condition or minimally impaired. However, in some areas these conditions no longer exist and may not be attainable. In these situations, the reference biological communities represent the best attainable conditions. In either case, the reference conditions then become the basis for developing biocriteria for major surface water types (streams, rivers, lakes, wetlands, estuaries, or marine waters).

Biological criteria support designated aquatic life use classifications for application in State standards (see chapter 2). Each State develops its own designated use classification system based on the generic uses cited in the Act (e.g., protection and propagation of fish, shellfish, and wildlife). Designated uses are intentionally general. However, States may develop subcategories within use designations to refine and clarify the use class. Clarification of the use class is particularly helpful when a variety of surface waters with distinct characteristics fit within the same use class, or do not fit well into any category.

For example, subcategories of aquatic life uses may be on the basis of attainable habitat (e.g., coldwater versus warmwater stream systems as represented by distinctive trout or bass fish communities, respectively). Special uses may also be designated to protect particularly unique, sensitive, or valuable aquatic species, communities, or habitats.

Resident biota integrate multiple impacts over time and can detect impairment from known and unknown causes. Biological criteria can be used to verify improvement in water quality in response to regulatory and other improvement efforts and to detect new or continuing degradation of waters. Biological criteria also provide a framework for developing improved best management practices and management measures for nonpoint source impacts. Numeric biological criteria can provide effective monitoring criteria for more definitive evaluation of the health of an aquatic ecosystem.

The assessment of the biological integrity of a water body should include measures of the structure and function of the aquatic community within a specified habitat. Expert knowledge of the system is required for the selection of appropriate biological components and measurement indices. The development and implementation of biological criteria requires:

- selection of surface waters to use in developing reference conditions for each designated use;
- measurement of the structure and function of aquatic communities in reference surface waters to establish biological criteria;
- measurement of the physical habitat and other environmental characteristics of the water resource; and
- establishment of a protocol to compare the biological criteria to biota in comparable test waters to determine whether impairment has occurred.

These elements serve as an interactive network that is particularly important during early development of biological criteria where rapid accumulation of information is effective for refining both designated uses and developing biological criteria values and the supporting biological monitoring and assessment techniques.

3.5.4 Sediment Criteria

While ambient water quality criteria are playing an important role in assuring a healthy aquatic environment, they alone have not been sufficient to ensure appropriate levels of environmental protection. Sediment contamination, which can involve deposition of toxicants over long periods of time, is responsible for water quality impacts in some areas.

EPA has authority to pursue the development of sediment criteria in streams, lakes and other waters of the United States under sections 104 and 304(a)(1) and (2) of the CWA as follows:

- section 104(n)(1) authorizes the Administrator to establish national programs that study the effects of pollution, including sedimentation, in estuaries on aquatic life;
- section 304(a)(1) directs the Administrator to develop and publish criteria for water quality, including information on the factors affecting rates of organic and inorganic sedimentation for varying types of receiving waters;
- section 304(a)(2) directs the Administrator to develop and publish information on, among other issues, "the factors necessary for the protection and propagation of shellfish, fish, and wildlife for classes and categories of receiving waters. . . ."

To the extent that sediment criteria could be developed that address the concerns of the section 404(b)(1) Guidelines for discharges of dredged or fill material under the CWA or the Marine Protection, Research, and Sanctuaries Act, they could also be incorporated into those regulations.

EPA's current sediment criteria development effort, as described below, focuses on criteria for the protection of aquatic life. EPA anticipates potential future expansion of this effort to include sediment criteria for the protection of human health.

Chemical Approach to Sediment Criteria Development

Over the past several years, sediment criteria development activities have centered on evaluating and developing the Equilibrium Partitioning Approach for generating sediment criteria. The Equilibrium Partitioning Approach focuses on predicting the chemical interaction between sediments and contaminants. Developing an understanding of the principal factors that influence the sediment/contaminant interactions will allow predictions to be made regarding the level of contaminant concentration that benthic and other organisms may be exposed to. Chronic water quality criteria, or possibly other toxicological endpoints, can then be used to predict potential biological effects. In addition to the development of sediment criteria, EPA is also working to develop a standardized sediment toxicity test that could be used with or independently of sediment criteria to assess chronic effects in fresh and marine waters.

> ***Equilibrium Partitioning (EqP) Sediment Quality Criteria (SQC) are the U.S. Environmental Protection Agency's best recommendation of the concentration of a substance in sediment that will not unacceptably affect benthic organisms or their uses.***

Methodologies for deriving effects-based SQC vary for different classes of compounds. For non-ionic organic chemicals, the methodology requires normalization to organic carbon. A methodology for deriving effects-based sediment criteria for metal contaminants is under development and is expected to require normalization to acid volatile sulfide. EqP SQC values can be derived for varying degrees of uncertainty and levels of protection, thus permitting use for ecosystem protection and remedial programs.

Application of Sediment Criteria

SQC would provide a basis for making more informed decisions on the environmental impacts of contaminated sediments. Existing sediment assessment methodologies are limited in their ability to identify chemicals of concern, responsible parties, degree of contamination, and zones of impact. To make the most informed decisions, EPA believes that a comprehensive approach using SQC and biological test methods is preferred.

Sediment criteria will be particularly valuable in site-monitoring applications where sediment contaminant concentrations are gradually approaching a criterion over time or as a preventive tool to ensure that point and nonpoint sources of contamination are controlled and that uncontaminated sediments remain uncontaminated. Also comparison of field measurements to sediment criteria will be a reliable method for providing early warning of a potential problem. An early warning would provide an opportunity to take corrective action before adverse impacts occur. For the reasons mentioned above, it has been identified that SQC are essential to resolving key contaminated sediment and source control issues in the Great Lakes.

Specific Applications

Specific applications of sediment criteria are under development. The primary use of EqP-based sediment criteria will be to assess risks associated with contaminants in sediments. The various offices and programs concerned with contaminated sediment have different regulatory mandates and, thus, have different needs and areas for potential application of sediment criteria. Because each regulatory need is different, EqP-based sediment quality criteria designed specifically to meet the needs of one office or program may have to be implemented in different ways to meet the needs of another office or program.

One mode of application of EqP-based numerical sediment quality criteria would be in a tiered approach. In such an application, when contaminants in sediments exceed the sediment quality criteria the sediments would be considered as causing unacceptable impacts. Further testing may or may not be required depending on site-specific conditions and the degree in which a criterion has been violated. (In locations where contamination significantly exceeds a criterion, no additional testing would be required. Where sediment contaminant levels are close to a criterion, additional testing might be necessary.) Contaminants in a sediment at concentrations less than the sediment criterion would not be of concern. However, in some cases the sediment could not be considered safe because it might contain other contaminants above safe levels for which no sediment criteria exist. In addition, the synergistic, antagonistic, or additive effects of several contaminants in the sediments may be of concern.

Additional testing in other tiers of an evaluation approach, such astoxicity tests, could be required to determine if the sediment is safe. It is likely that such testing would incorporate site-specific considerations. Examples of specific applications of sediment criteria after they are developed include the following:

- Establish permit limits for point sources to ensure that uncontaminated sediments remain uncontaminated or sediments already contaminated have an opportunity to cleanse themselves. Of course, this would occur only after criteria and the means to tie point sources to sediment contamination are developed.

- Establish target levels for nonpoint sources of sediment contamination.

- For remediation activities, SQC would be valuable in identifying:

  - need for remediation,

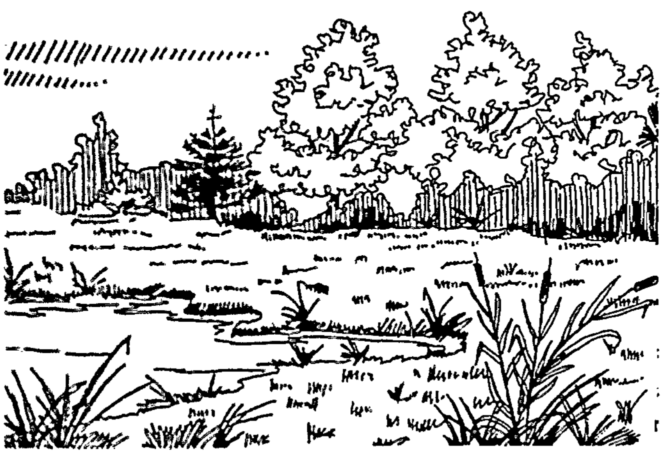
  - spatial extent of remediation area,

  - benefits derived from remediation activities,

  - responsible parties,

  - impacts of depositing contaminated sediments in water environments, and

  - success of remediation activities.



In tiered testing sediment evaluation processes, sediment criteria and biological testing procedures work very well together.

Sediment Criteria Status

Science Advisory Board Review

The Science Advisory Board has completed a second review of the EqP approach to deriving sediment quality criteria for non-ionic contaminants. The November 1992 report (USEPA, 1992c) endorses the EqP approach to deriving criteria as ". . . sufficiently valid to be used in the regulatory process if the uncertainty associated with the method is considered, described, and incorporated," and that "EPA should . . . establish criteria on the basis of present knowledge within the bounds of uncertainty. . . ."

The Science Advisory Board also identified the need for ". . . a better understanding of the uncertainty around the assumptions inherent in the approach, including assumptions of equilibrium, bioavailability, and kinetics, all critical to the application of the EqP."

Sediment Criteria Documents and Application Guidance

EPA efforts at producing sediment criteria documents are being directed first toward phenanthrene, fluoranthene, dieldrin, acenaphthene, and endrin. Efforts are also being directed towards producing a guidance document on the derivation and interpretation of sediment quality criteria. The criteria documents were announced in the *Federal Register* in January 1994; the public comment period ended June 1994. Final documents and implementation guidance should be available in early 1996.

Methodology for Developing Sediment Criteria for Metal Contaminants

EPA is proceeding to develop a methodology for calculating sediment criteria for benthic toxicity to metal contaminants, with key work focused on identifying and understanding the role of acid volatile sulfides (AVS), and other binding factors, in controlling the bioavailability of metal contaminants. A variety of field and laboratory verification studies are under way to add additional support to the methodology. Standard AVS sampling and analytical procedures are under development. Presentation of the metals methodology to the SAB for review is anticipated for Fall 1994.

Biological Approach to Sediment Criteria Development

Under the Contaminated Sediment Management Strategy, EPA programs have committed to using consistent biological methods to determine if sediments are contaminated. In the water program, these biological methods will be used as a complement to the sediment-chemical criteria under development. The biological methods consist of both toxicity and bioaccumulation tests. Freshwater and saltwater benthic species, selected to represent the sensitive range of species' responses to toxicity, are used in toxicity tests to measure sediment toxicity. Insensitive freshwater and saltwater benthic species that form the base of the food chain are used in toxicity tests to measure the bioaccumulation potential of sediment. In FY 1994, acute toxicity tests and bioaccumulation tests selected by all the Agency programs should be standardized and available for use. Training for States and EPA Regions on these methods is expected to begin in FY1995.

In the next few years, research will be conducted to develop standardized chronic toxicity tests for sediment as well as toxicity identification evaluation (TIE) methods. The TIE approach will be used to identify the specific chemicals in a sediment causing acute or chronic toxicity in the test organisms. Under the Contaminated Sediment Management Strategy, EPA's programs have also agreed to incorporate these chronic toxicity and TIE methods into their sediment testing when they are available.

3.5.5 Wildlife Criteria

Terrestrial and avian species are useful as sentinels for the health of the ecosystem as a whole. In many cases, damage to wildlife indicates that the ecosystem itself is damaged. Many wildlife species that are heavily dependent on the aquatic food web reflect the health of aquatic systems. In the case of toxic chemicals, terminal predators such as otter, mink, gulls, terns, eagles, ospreys, and turtles are useful as integrative indicators of the status or health of the ecosystem.

Statutory and Regulatory Authority

Section 101(a)(2) of the CWA sets, as an interim goal of,

> . . . wherever attainable . . . water quality which provides for the protection and propagation of fish, shellfish, and <u>wildlife</u> . . . (emphasis added).

Section 304(a)(1) of the Act also requires EPA to:

> . . . develop and publish . . . criteria for water quality accurately reflecting . . . the kind and extent of all identifiable effects on health and welfare including . . . wildlife.

The Water Quality Standards Regulation reflect the statutory goals and requirements by requiring States to adopt, where attainable, the CWA section 101(a)(2) goal uses of protection and propagation of fish, shellfish, and wildlife (40 CFR 131.10), and to adopt water quality criteria sufficient to protect the designated use (40 CFR 131.11).

Wildlife Protection in Current Aquatic Criteria

Current water quality criteria methodology is designed to protect fish, benthic invertebrates, and zooplankton; however, there is a provision in the current aquatic life criteria guidelines (Appendix H) that is intended to protect wildlife that consume aquatic organisms from the bioaccumulative potential of a compound. The final residue value can be based on either the FDA Action Level or a wildlife feeding study. However, if maximum permissible tissue concentration is not available from a wildlife feeding study, a final residue value cannot be derived and the criteria quantification procedure continues without further consideration of wildlife impacts. Historically, wildlife have been considered only after detrimental effects on wildlife populations have been observed in the environment (this occurred with relationship to DDT, selenium, and PCBs).

Wildlife Criteria Development

EPA's national wildlife criteria effort began following release of a 1987 Government Accounting Office study entitled *Wildlife Management - National Refuge Contamination Is Difficult To Confirm and Clean Up* (GAO, 1987). After waterfowl deformities observed at Kesterson Wildlife Refuge were linked to selenium contamination in the water, Congress requested this study and recommended that "the Administrator of EPA, in close coordination with the Secretary of the Interior, develop water quality criteria for protecting wildlife and their refuge habitat."

In November of 1988, EPA's Environmental Research Laboratory in Corvallis sponsored a workshop entitled *Water Quality Criteria To Protect Wildlife Resources*, (USEPA, 1989g) which was co-chaired by EPA and the Fish and Wildlife Service (FWS). The workshop brought together 26 professionals from a variety of institutions, including EPA, FWS, State governments, academia, and consultants who had expertise in wildlife toxicity, aquatic toxicity, ecology, environmental risk assessment, and conservation. Efforts at he workshop focused on evaluating the need for, and developing a strategy for production of wildlife criteria. Two recommendations came out of that workshop:

(1) The process by which ambient water quality criteria are established should be modified to consider effects on wildlife; and

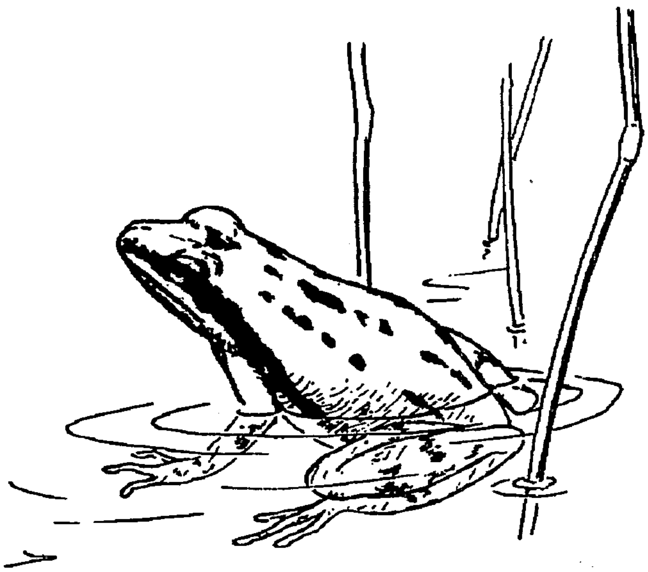
(2) chemicals should be prioritized based on their potential to adversely impact wildlife species.

Based on the workshop recommendations, screening level wildlife criteria (SLWC) were calculated for priority pollutants and chemicals of concern submitted by the FWS to gauge the extent of the problem by:

(1) evaluating whether existing water quality criteria for aquatic life are protective of wildlife, and

(2) prioritizing chemicals for their potential to adversely impact wildlife species.

There were 82 chemicals for which EPA had the necessary toxicity information as well as ambient water quality criteria, advisories, or lowest-observed-adverse-effect levels (LOAELs) to compare with the SLWC values. As would be expected, the majority of chemicals had SLWC larger than existing water quality criteria, advisories, or LOAELs for aquatic life. However, the screen identified classes of compounds for which current ambient water quality criteria may not be adequately protective of wildlife: chlorinated alkanes, benzenes, phenols, metals, DDT, and dioxins. Many of these compounds are produced in very large amounts and have a variety of uses (e.g., solvents, flame retardants, organic syntheses of fungicides and herbicides, and manufacture of plastics and textiles. The manufacture and use of



these materials produce waste byproduct). Also, 5 of the 21 are among the top 25 pollutants identified at Superfund sites in 1985 (3 metals, 2 organics).

Following this initial effort, EPA held a national meeting in April 1992[1] to constructively discuss and evaluate proposed methodologies for deriving wildlife criteria to build consensus among the scientific community as to the most defensible scientifically approach(es) to be pursued by EPA in developing useful and effective wildlife criteria.

The conclusions of this national meeting were as follows:

- wildlife criteria should have a tissue-residue component when appropriate;
- peer-review of wildlife criteria and data sets should be used in their derivation;
- wildlife criteria should incorporate methods to establish site-specific wildlife criteria;
- additional amphibian and reptile toxicity data are needed;
- further development of inter-species toxicological sensitivity factors are needed; and
- criteria methods should measure biomarkers in conjunction with other studies.

On April 16, 1993, EPA proposed wildlife criteria in the *Water Quality Guidance for the Great Lakes System* (58 F.R. 20802). The proposed wildlife criteria are based on the current EPA noncancer human health criteria approach. In this proposal, in addition to requesting comments on the proposed Great Lakes criteria and methods, EPA also requested comments on possible modifications of the proposed Great Lakes approach for consideration in the development of national wildlife criteria.

3.5.6 Numeric Criteria for Wetlands

Extension of the EPA national 304(a) numeric aquatic life criteria to wetlands is recommended as part of a program to develop standards and criteria for wetlands. Appendices D and E provide an overview of the need for standards and criteria for wetlands. The 304(a) numeric aquatic life criteria are designed to be protective of aquatic life for surface waters and are generally applicable to most wetland types. Appendix E provides a possible approach, based on the site-specific guidelines, for detecting wetland types that might not be protected by direct application of national 304(a) criteria. The evaluation can be simple and inexpensive for those wetland types for which sufficient water chemistry and species assemblage data are available, but will be less useful for wetland types for which these data are not readily available. In Appendix E, the site-specific approach is described and recommended for wetlands for which modification of the 304(a) numeric criteria are considered necessary. The results of this type of evaluation, combined with information on local or regional environmental threats, can be used to prioritize wetland types (and individual criteria) for further site-specific evaluations and/or additional data collection. Close coordination among regulatory agencies, wetland scientists, and criteria experts will be required.

3.6 Policy on Aquatic Life Criteria for Metals

It is the policy of the Office of Water that the use of dissolved metal to set and measure compliance with water quality standards is the recommended approach, because dissolved metal more closely approximates the bioavailable fraction of metal in the water column than does total recoverable metal. This conclusion regarding metals bioavailability is supported by a majority of the scientific community within and outside EPA. One reason is that a primary mechanism for water column toxicity is adsorption at the gill surface which requires metals to be in the dissolved form.

Until the scientific uncertainties are better resolved, a range of different risk management decisions can be justified by a State. EPA recommends that State water quality standards be based on dissolved metal--a conversion factor must be used in order to express the EPA criteria articulated as total recoverable as dissolved. (See the paragraph below for technical details on developing dissolved criteria.) EPA will also approve a State risk management decision to adopt standards based on total recoverable metal, if those standards are otherwise approvable as a matter of law. (*Office of Water Policy and Technical Guidance on Interpretation and Implementation of Aquatic Life Metals Criteria* USEPA, 1993f)

3.6.1 Background

The implementation of metals criteria is complex due to the site-specific nature of metals toxicity. This issue covers a number of areas including the expression of aquatic life criteria; total maximum daily loads (TMDLs), permits, effluent monitoring, and compliance; and ambient monitoring. The following Sections, based on the policy memorandum referenced above, provide additional guidance in each of these areas. Included in this Handbook as Appendix J are three guidance documents issued along with the Office of Water policy memorandum with additional technical details. They are: *Guidance Document on Expression of Aquatic Life Criteria as Dissolved Criteria* (Attachment #2), *Guidance Document on Dynamic Modeling and Translators* (Attachment #3), and *Guidance Document on Monitoring* (Attachment #4). These will be supplemented as additional information becomes available.

Since metals toxicity is significantly affected by site-specific factors, it presents a number of programmatic challenges. Factors that must be considered in the management of metals in the aquatic environment include: toxicity specific to effluent chemistry; toxicity specific to ambient water chemistry; different patterns of toxicity for different metals; evolution of the state of the science of metals toxicity, fate, and transport; resource limitations for monitoring, analysis, implementation, and research functions; concerns regarding some of the analytical data currently on record due to possible sampling and analytical contamination; and lack of standardized protocols for clean and ultraclean metals analysis. The States have the key role in the risk management process of balancing these factors in the management of water programs. The site-specific nature of this issue could be perceived as requiring a permit-by-permit approach to implementation. However, EPA believes that this guidance can be effectively implemented on a broader level, across any waters with roughly the same physical and chemical characteristics, and recommends that States work with the EPA with that perspective in mind.

3.6.2 Expression of Aquatic Life Criteria

Dissolved vs. Total Recoverable Metal

A major issue is whether, and how, to use dissolved metal concentrations ("dissolved metal") or total recoverable metal concentrations ("total recoverable metal") in setting State water quality standards. In the past, States have used both approaches when applying the same EPA Section 304(a) criteria guidance. Some older criteria documents may have facilitated these different approaches to interpretation of the criteria because the documents were somewhat equivocal with regards to analytical methods. The May 1992 interim guidance continued the policy that either approach was acceptable.

The position that the dissolved metals approach is more accurate has been questioned because it neglects the possible toxicity of particulate metal. It is true that some studies have indicated that particulate metals appear to contribute to the toxicity of metals, perhaps because of factors such as desorption of metals at the gill surface, but these same studies indicate the toxicity of particulate metal is substantially less than that of dissolved metal.

Furthermore, any error incurred from excluding the contribution of particulate metal will generally be compensated by other factors which make criteria conservative. For example, metals in toxicity tests are added as simple salts to relatively clean water. Due to the likely presence of a significant concentration of metals binding agents in many discharges and ambient waters, metals in toxicity tests would generally be expected to be more bioavailable than metals in discharges or in ambient waters.

If total recoverable metal is used for the purpose of specifying water quality standards, the lower bioavailability of particulate metal and lower bioavailability of sorbed metals as they are discharged may result in an overly conservative water quality standard. The use of dissolved metal in water quality standards gives a more accurate result in the water column. However, total recoverable measurements in ambient water have value, in that exceedences of criteria on a total recoverable basis are an indication that metal loadings could be a stress to the ecosystem, particularly in locations other than the water column (*e.g.*, in the sediments).

The reasons for the potential consideration of total recoverable measurements include risk management considerations not covered by evaluation of water column toxicity alone. The ambient water quality criteria are neither designed nor intended to protect sediments, or to prevent effects in the food webs containing sediment dwelling organisms. A risk manager, however, may consider sediments and food chain effects and may decide to take a conservative approach for metals, considering that metals are very persistent chemicals. This conservative approach could include the use of total recoverable metal in water quality standards. However, since consideration of sediment impacts is not incorporated into the criteria methodology, the degree of conservatism inherent in the total recoverable approach is unknown. The uncertainty of metal impacts in sediments stem from the lack of sediment criteria and an imprecise understanding of the fate and transport of metals. EPA will continue to pursue research and other activities to close these knowledge gaps.

Dissolved Criteria

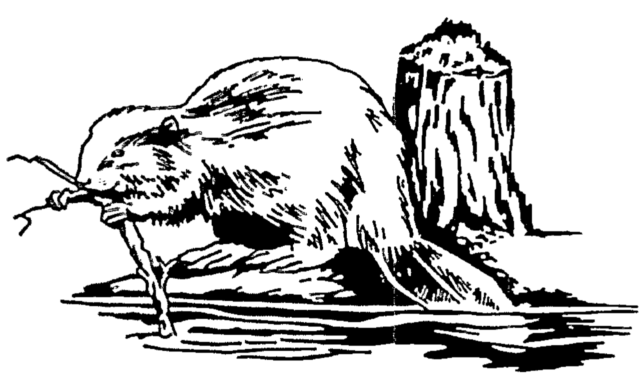
In the toxicity tests used to develop EPA metals criteria for aquatic life, some fraction of the metal is dissolved while some fraction is bound to particulate matter. The present criteria were developed using total recoverable metal measurements or measures expected to give equivalent results in toxicity tests, and are articulated as total recoverable. Therefore, in order to express the EPA criteria as dissolved, a total recoverable to dissolved conversion factor must be used. Attachment #2 in Appendix J provides guidance for calculating EPA dissolved criteria from the published total recoverable criteria. The data expressed as percentage metal dissolved are presented as recommended values and ranges. However, the choice within ranges is a State risk management decision. EPA has recently supplemented the data for copper and is proceeding to further supplement the data for copper and other metals. As testing is completed, EPA will make this information available and this is expected to reduce the magnitude of the ranges for some of the conversion factors provided. EPA also strongly encourages the application of dissolved criteria across a watershed or waterbody, as technically sound and the best use of resources.

Site-Specific Criteria Modifications

While the above methods will correct some site-specific factors affecting metals toxicity, further refinements are possible. EPA has issued guidance for three site-specific criteria development methodologies: recalculation procedure, water-effect ratio (WER) procedure (called the indicator species procedure in previous guidance) and resident species procedure. (See Section 3.7 of this Chapter.)

In the National Toxics Rule (57 FR 60848, December 22, 1992), EPA recommended the WER as an optional method for site-specific criteria development for certain metals. EPA committed in the NTR preamble to provide additional guidance on determining the WERs. The *Interim Guidance on the Determination and Use of Water-Effect Ratios for Metals* was issued by EPA on February 22, 1994 and is intended to fulfill that commitment. This interim guidance supersedes all guidance concerning water-effect ratios and the recalculation procedure previously issued by EPA. This guidance is included as Appendix L to this Handbook.

In order to meet current needs, but allow for changes suggested by protocol users, EPA issued the guidance as "interim." EPA will accept WERs developed using this guidance, as well as by using other scientifically defensible protocols.



3.6.3 Total Maximum Daily Loads (TMDLs) and National Pollutant Discharge Elimination System (NPDES) Permits

Dynamic Water Quality Modeling

Although not specifically part of the reassessment of water quality criteria for metals, dynamic or probabilistic models are another useful tool for implementing water quality criteria, especially for those criteria protecting aquatic life. These models provide another way to incorporate site-specific data. The *Technical Support Document for Water Quality-based Toxics Control* (TSD) (USEPA, 1991a) describes dynamic, as well as static (steady-state) models. Dynamic models make the best use of the specified magnitude, duration, and frequency of water quality criteria and, therefore, provide a more accurate representation of the probability that a water quality standard exceedence will occur. In contrast, steady-state models frequently apply a number of simplifying, worst case assumptions which makes them less complex but also less accurate than dynamic models.

Dynamic models have received increased attention over the last few years as a result of the widespread belief that steady-state modeling is over-conservative due to environmentally conservative dilution assumptions. This belief has led to the misconception that dynamic models will always lead to less stringent regulatory controls (e.g., NPDES effluent limits) than steady-state models, which is not true in every application of dynamic models. EPA considers dynamic models to be a <u>more accurate</u> approach to implementing water quality criteria and continues to recommend their use. Dynamic modeling does require a commitment of resources to develop appropriate data. (See Appendix J, Attachment #3 and the USEPA, 1991a for details on the use of dynamic models.)

Dissolved-Total Metal Translators

Expressing ambient water quality criteria for metals as the dissolved form of a metal poses a need to be able to translate from dissolved metal to total recoverable metal for TMDLs and NPDES permits. TMDLs for metals must be able to calculate: (1) dissolved metal in order to ascertain attainment of water quality standards, and (2) total recoverable metal in order to achieve mass balance necessary for permitting purposes.

EPA's NPDES regulations require that limits of metals in permits be stated as total recoverable in most cases (see 40 CFR §122.45(c)) except when an effluent guideline specifies the limitation in another form of the metal, the approved analytical methods measure only dissolved metal, or the permit writer expresses a metals limit in another form (e.g., dissolved, valent specific, or total) when required to carry out provisions of the Clean Water Act. This is because the chemical conditions in ambient waters frequently differ substantially from those in the effluent, and there is no assurance that effluent particulate metal would not dissolve after discharge. The NPDES rule does not require that State water quality standards be expressed as total recoverable; rather, the rule requires permit writers to translate between different metal forms in the calculation of the permit limit so that a total recoverable limit can be established. Both the TMDL and NPDES uses of water quality criteria require the ability to translate between dissolved metal and total recoverable metal. Appendix J, Attachment #3 provides guidance on this translation.

3.6.4 Guidance on Monitoring

Use of Clean Sampling and Analytical Techniques

In assessing waterbodies to determine the potential for toxicity problems due to metals, the quality of the data used is an important issue. Metals data are used to determine attainment status for water quality standards, discern trends in water quality, estimate background loads for TMDLs, calibrate fate and transport models, estimate effluent concentrations (including effluent variability), assess permit compliance, and conduct research. The quality of trace level metal data, especially below 1 ppb, may be compromised due to contamination of samples during collection, preparation, storage, and analysis. Depending on the level of metal present, the use of "clean" and "ultraclean" techniques for sampling and analysis may be critical to accurate data for implementation of aquatic life criteria for metals.

The significance of the sampling and analysis contamination problem increases as the ambient and effluent metal concentration decreases and, therefore, problems are more likely in ambient measurements. "Clean" techniques refer to those requirements (or practices for sample collection and handling) necessary to produce reliable analytical data in the part per billion (ppb) range. "Ultraclean" techniques refer to those requirements or practices necessary to produce reliable analytical data in the part per trillion (ppt) range. Because typical concentrations of metals in surface waters and effluents vary from one metal to another, the effect of contamination on the quality of metals monitoring data varies appreciably.

EPA plans to develop protocols on the use of clean and ultra-clean techniques and is coordinating with the United States Geological Survey (USGS) on this project, because USGS has been doing work on these techniques for some time, especially the sampling procedures. Draft protocols for clean techniques were presented at the Norfolk, VA analytical methods conference in the Spring of 1994 and final protocols are expected to be available in early 1995. The development of comparable protocols for ultra-clean techniques is underway and are expected to be available in late 1995. In developing these protocols, we will consider the costs of these techniques and will give guidance as to the situations where their use is necessary. Appendix L, pp. 98-108 provide some general guidance on the use of clean analytical techniques. We recommend that this guidance be used by States and Regions as an interim step, while the clean and ultra-clean protocols are being developed.

Use of Historical Data

The concerns about metals sampling and analysis discussed above raise corresponding concerns about the validity of historical data. Data on effluent and ambient metal concentrations are collected by a variety of organizations including Federal agencies (e.g., EPA, USGS), State pollution control agencies and health departments, local government agencies, municipalities, industrial dischargers, researchers, and others. The data are collected for a variety of purposes as discussed above.

Concern about the reliability of the sample collection and analysis procedures is greatest where they have been used to monitor very low level metal concentrations. Specifically, studies have shown data sets with contamination problems during sample collection and laboratory analysis, that have resulted in inaccurate measurements. For example, in developing a TMDL for New York Harbor, some historical ambient data showed extensive metals problems in the harbor, while other historical ambient data showed only limited metals problems. Careful resampling and analysis in 1992/1993 showed the latter view was correct. The key to producing accurate data is appropriate quality assurance (QA) and quality control (QC) procedures. EPA believes that most historical data for metals, collected and analyzed with appropriate QA and QC at levels of 1 ppb or higher, are reliable. The data used in development of EPA criteria are also considered reliable, both because they meet the above test and because the toxicity test solutions are created by adding known amounts of metals.

With respect to effluent monitoring reported by an NPDES permittee, the permittee is responsible for collecting and reporting quality data on a Discharge Monitoring Report (DMR). Permitting authorities should continue to consider the information reported to be true, accurate, and complete as certified by the permittee. Where the permittee becomes aware of new information specific to the effluent discharge that questions the quality of previously submitted DMR data, the permittee must promptly submit that information to the permitting authority. The permitting authority will consider all information submitted by the permittee in determining appropriate enforcement responses to monitoring/reporting and effluent violations. (See Appendix J, Attachment #4 for additional details.)

3.7 Site-Specific Aquatic Life Criteria

The purpose of this section is to provide guidance for the development of site-specific water quality criteria which reflect local environmental conditions. Site-specific criteria are allowed by regulation and are subject to EPA review and approval. The Federal water quality standards regulation at section 131.11(b)(1)(ii) provides States with the opportunity to adopt water quality criteria that are "...modified to reflect site-specific conditions." Site-specific criteria, as with all water quality criteria, must be based on a sound scientific rationale in order to protect the designated use. Existing guidance and practice are that EPA will approve site-specific criteria developed using appropriate procedures.

A site-specific criterion is intended to come closer than the national criterion to providing the intended level of protection to the aquatic life at the site, usually by taking into account the biological and/or chemical conditions (i.e., the species composition and/or water quality characteristics) at the site. The fact that the U.S. EPA has made these procedures available should not be interpreted as implying that the agency advocates that states derive site-specific criteria before setting state standards. Also, derivation of a site-specific criterion does not change the intended level of protection of the aquatic life at the site.

3.7.1 History of Site-Specific Criteria Guidance

National water quality criteria for aquatic life may be under- or over-protective if:

(1) the species at the site are more or less sensitive than those included in the national criteria data set (*e.g.*, the national criteria data set contains data for trout, salmon, penaeid shrimp, and other aquatic species that have been shown to be especially sensitive to some materials), or

(2) physical and/or chemical characteristics of the site alter the biological availability and/or toxicity of the chemical (*e.g.*, alkalinity, hardness, pH, suspended solids and salinity influence the concentration(s) of the toxic form(s) of some heavy metals, ammonia and other chemicals).

Therefore, it is appropriate that site-specific procedures address each of these conditions separately as well as the combination of the two. In the early 1980's, EPA recognized that laboratory-derived water quality criteria might not accurately reflect site-specific conditions and, in response, created three procedures to derive site-specific criteria. This Handbook contains the details of these procedures, referenced below.

1. The Recalculation Procedure is intended to take into account relevant differences between the sensitivities of the aquatic organisms in the national dataset and the sensitivities of organisms that occur at the site (see Appendix L, pp. 90-97).

2. The Water-Effect Ratio Procedure (called the Indicator Species Procedure in USEPA, 1983a; 1984f) provided for the use of a water-effect ratio (WER) that is intended to take into account relevant differences between the toxicities of the chemical in laboratory dilution water and in site water (see Appendix L).

3. The Resident Species Procedure intended to take into account both kinds of differences simultaneously (see Section 3.7.6).

These procedures were first published in the 1983 *Water Quality Standards Handbook* (USEPA, 1983a) and expanded upon in the *Guidelines for Deriving Numerical Aquatic Site-Specific Water Quality Criteria by Modifying National Criteria* (USEPA, 1984f). Interest has increased in recent years as states have devoted more attention to chemical-specific water quality criteria for aquatic life. In addition, interest in water-effect ratios increased when they were integrated into some of the aquatic life criteria for metals that were promulgated for several states in the National Toxics Rule (57 FR 60848, December 22, 1992). The *Office of Water Policy and Technical Guidance on Interpretation and Implementation of Aquatic Life Criteria for Metals* (USEPA, 1993f) (see Section 3.6 of this Handbook) provided further guidance on site-specific criteria for metals by recommending the use of dissolved metals for setting and measuring compliance with water quality standards.

The early guidance concerning WERs (USEPA, 1983a; 1984f) contained few details and needed revision, especially to take into account newer guidance concerning metals. To meet this need, EPA issued *Interim Guidance on the Determination and Use of Water-Effect Ratios for Metals* in 1994 (Appendix L). Metals are specifically addressed in Appendix L because of the National Toxics Rule and because of current interest in aquatic life criteria for metals; although most of this guidance also applies to other pollutants, some obviously applies only to metals. Appendix L supersedes all guidance concerning water-effect ratios and the Indicator Species Procedure given in Chapter 4 of the *Water Quality Standards Handbook* (USEPA, 1983a) and in *Guidelines for Deriving Numerical Aquatic Site-Specific Water Quality Criteria by Modifying National Criteria* (USEPA, 1984f). Appendix L (p. 90-98) also supersedes the guidance in these earlier documents for the Recalculation Procedure for performing site-specific criteria modifications. The Resident Species Procedure remains essentially unchanged since 1983 (except for changes in the averaging periods to conform to the 1985 aquatic life criteria guidelines (USEPA, 1985b) and is presented in Section 3.7.6, below.

The previous guidance concerning site-specific procedures did not allow the Recalculation Procedure and the WER procedure to be used together in the derivation of a site-specific aquatic life criterion; the only way to take into account both species composition and water quality characteristics in the determination of a site-specific criterion was to use the Resident Species Procedure. A specific change contained Appendix L is that, except in jurisdictions that are subject to the National Toxics Rule, the Recalculation Procedure and the WER Procedure may now be used together provided that the recalculation procedure is performed first. Both the Recalculation Procedure and the WER Procedure are based directly on the guidelines for deriving national aquatic life criteria (USEPA 1985) and, when the two are used together, use of the Recalculation Procedure must be performed first because the Recalculation Procedure has specific implications concerning the determination of the WER.

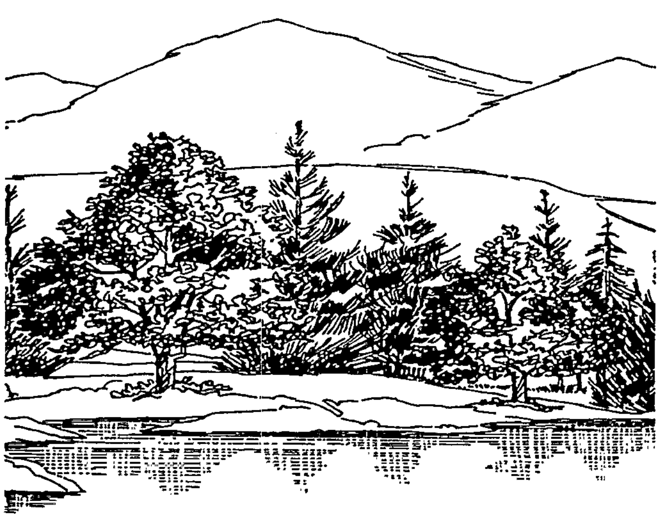
3.7.2 Preparing to Calculate Site-Specific Criteria

Adopting site-specific criteria in water quality standards is a State option--not a requirement. Moreover, EPA is not advocating that States use site-specific criteria development procedures for setting all aquatic life criteria as opposed to using the National Section 304(a) criteria recommendations. Site-specific criteria are not needed in all situations. When a State considers the possibility of developing site-specific criteria, it is essential to involve the appropriate EPA Regional office at the start of the project.

This early planning is also essential if it appears that data generation and testing may be conducted by a party other than the State or EPA. The State and EPA need to apply the procedures judiciously and must consider the complexity of the problem and the extent of knowledge available concerning the fate and effect of the pollutant under consideration. If site-specific criteria are developed without early EPA involvement in the planning and design of the task, the State may expect EPA to take additional time to closely scrutinize the results before granting any approval to the formally adopted standards.

The following sequence of decisions need to be made before any of the procedures are initiated:

- verify that site-specific criteria are actually needed (*e.g.*, that the use of clean sampling and/or analytical techniques, especially for metals, do not result in attainment of standards.)
- Define the site boundaries.
- Determine from the national criterion document and other sources if physical and/or chemical characteristics are known to affect the biological availability and/or toxicity of a material of interest.
- If data in the national criterion document and/or from other sources indicate that the range of sensitivity of the selected resident species to the material of interest is different from the range for the species in the national criterion document, and variation in physical and/or chemical characteristics of the site water is not expected to be a factor, use the *Recalculation Procedure* (Section 3.7.4).



- If data in the national criterion document and/or from other sources indicate that physical and/or chemical characteristics of the site water may affect the biological availability and/or toxicity of the material of interest, and the selected resident species range of sensitivity is <u>similar</u> to that for the species in the national criterion document, use the *Water-Effect Ratio Procedure* (Section 3.7.5).

- If data in the national criterion document and/or from other sources indicated that physical and/or chemical characteristics of the site water may affect the biological availability and/or toxicity of the material of interest, and the selected resident species range of sensitivity is <u>different</u> from that for the species in the national criterion document, and if both these differences are to be taken into account, use the *Recalculation Procedure in conjunction with the Water-Effect Ratio Procedure* or use the *Resident Species Procedure* (Section 3.7.6).

3.7.3 Definition of a Site

Since the rationales for site-specific criteria are usually based on potential differences in species sensitivity, physical and chemical characteristics of the water, or a combination of the two, the concept of site must be consistent with this rationale.

In the general context of site-specific criteria, a "site" may be a state, region, watershed, waterbody, or segment of a waterbody. The site-specific criterion is to be derived to provide adequate protection for the entire site, however the site is defined.

If water quality effects on toxicity are not a consideration, the site can be as large as a generally consistent biogeographic zone permits. For example, large portions of the Chesapeake Bay, Lake Michigan, or the Ohio River may be considered as one site if their respective aquatic communities do not vary substantially. However, when a site-specific criterion is derived using the Recalculation Procedure, all species that "occur at the site" need to be taken into account when deciding what species, if any, are to be deleted from the dataset. Unique populations or less sensitive uses within sites may justify a designation as a distinct site.

If the species of a site are toxicologically comparable to those in the national criteria data set for a material of interest, and physical and/or chemical water characteristics are the only factors supporting modification of the national criteria, then the site can be defined on the basis of expected changes in the material's biological availability and/or toxicity due to physical and chemical variability of the site water. However, when a site-specific criterion is derived using a WER, the WER is to be adequately protective of the entire site. If, for example, a site-specific criterion is being derived for an estuary, WERs could be determined using samples of the surface water obtained from various sampling stations, which, to avoid confusion, should not be called "sites". If all the WERs were sufficiently similar, one site-specific criterion could be derived to apply to the whole estuary. If the WERs were sufficiently different, either the lowest WER could be used to derive a site-specific criterion for the whole estuary, or the data might indicate that the estuary should be divided into two or more sites, each with its own criterion.

3.7.4 The Recalculation Procedure

The Recalculation Procedure is intended to cause a site-specific criterion to appropriately differ from a national aquatic life criterion if justified by demonstrated pertinent toxicological differences between the aquatic species that occur at the site and those that were used in the derivation of the national criterion. There are at least three reasons why such differences might exist between the two sets of species.

- First, the national dataset contains aquatic species that are sensitive to many pollutants, but these and comparably sensitive species might not occur at the site.

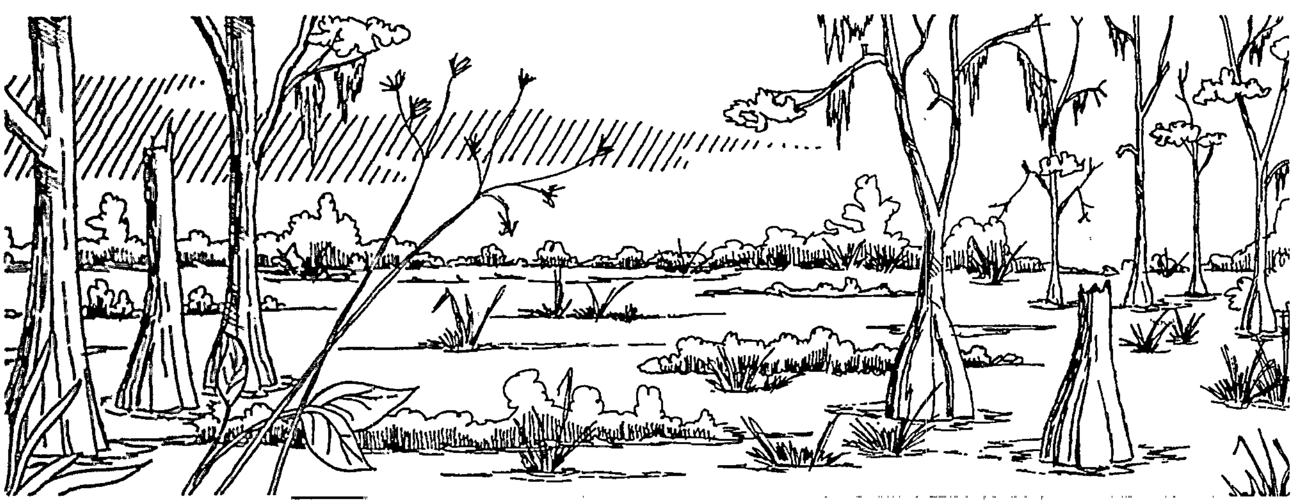
- Second, a species that is critical at the site might be sensitive to the pollutant and require a lower criterion. (A critical species is a species that is commercially or recreationally important at the site, a species that exists at the site and is listed as threatened or endangered under section 4 of the Endangered Species Act, or a species for which there is evidence that the loss of the species from the site is likely to cause an unacceptable impact on a commercially or recreationally important species, a threatened or endangered species, the abundances of a variety of other species, or the structure or function of the community.)

- Third, the species that occur at the site might represent a narrower mix of species than those in the national dataset due to a limited range of natural environmental conditions.

The procedure presented in Appendix L, pp. 90-98 is structured so that corrections and additions can be made to the national dataset without the deletion process being used to take into account taxa that do not occur at the site; in effect, this procedure makes it possible to update the national aquatic life criterion. All corrections and additions that have been approved by EPA are required, whereas use of the deletion process is optional. The deletion process may not be used to remove species from the criterion calculation that are not currently present at a site due to degraded conditions.

The Recalculation Procedure is more likely to result in lowering a criterion if the net result of addition and deletion is to decrease the number of genera in the dataset, whereas the procedure is more likely to result in raising a criterion if the net result of addition and deletion is to increase the number of genera in the dataset.

For the lipid soluble chemicals whose national Final Residue Values are based on Food and Drug Administration (FDA) action levels, adjustments in those values based on the percent lipid content of resident aquatic species is appropriate for the derivation of site-specific Final Residue Values. For lipid-soluble materials, the national Final Residue Value is based on an average 11 percent lipid content for edible portions for the freshwater chinook salmon and lake trout and an average of 10 percent lipids for the edible portion for saltwater Atlantic herring. Resident species of concern may have higher (e.g., Lake Superior siscowet, a race of lake trout) or lower (e.g., many sport fish) percent lipid content than used for the national Final Residue Value.



For some lipid-soluble materials such as polychlorinated biphenyls (PCB) and DDT, the national Final Residue Value is based on wildlife consumers of fish and aquatic invertebrate species rather than an FDA action level because the former provides a more stringent residue level. See the National Guidelines (USEPA, 1985b) for details.

For the lipid-soluble materials whose national Final Residue Values are based on wildlife effects, the limiting wildlife species (mink for PCB and brown pelican for DDT) are considered acceptable surrogates for resident avian and mammalian species (e.g., herons, gulls, terns, otter, etc.) Conservatism is appropriate for those two chemicals, and no less restrictive modification of the national Final Residue Value is appropriate. The site-specific Final Residue Value would be the same as the national value.

3.7.5 The Water-Effect Ratio (WER) Procedure

The guidance on the Water-Effect Ratio Procedure presented in Appendix L is intended to produce WERs that may be used to derive site-specific aquatic life criteria from most national and state aquatic life criteria that were derived from laboratory toxicity data.

As indicated in Appendix L, the determination of a water-effect ratio may require substantial resources. A discharger should consider cost-effective, preliminary measures described in this Appendix L (e.g., use of "clean" sampling and chemical analytical techniques especially for metals, or in non-NTR States, a recalculated criterion) to determine if an indicator species site-specific criterion is really needed. In many instances, use of these other measures may eliminate the need for deriving water-effect ratios. The methods described in the 1994 interim guidance (Appendix L) should be sufficient to develop site-specific criteria that resolve concerns of dischargers when there appears to be no instream toxicity but, where (a) a discharge appears to exceed existing or proposed water quality-based permit limits, or (b) an instream concentration appears to exceed an existing or proposed water quality criterion.

WERs obtained using the methods described in Appendix L should only be used to adjust aquatic life criteria that were derived using laboratory toxicity tests. WERs determined using the methods described herein cannot be used to adjust the residue-based mercury Criterion Continuous Concentration (CCC) or the field-based selenium freshwater criterion.

Except in jurisdictions that are subject to the NTR, the WERs may also be used with site-specific aquatic life criteria that are derived using the Recalculation Procedure described in Appendix L (p.90).

Water-Effect Ratios in the Derivation of Site-Specific Criteria

A central question concerning WERs is whether their use by a State results in a site-specific criterion subject to EPA review and approval under Section 303(c) of the Clean Water Act?

Derivation of a water-effect ratio by a State is a site-specific criterion adjustment subject to EPA review and approval/disapproval under Section 303(c). There are two options by which this review can be accomplished.

Option 1:

A State may derive and submit each individual water-effect ratio determination to EPA for review and approval. This would be accomplished through the normal review and revision process used by a State.

Option 2:

A State can amend its water quality standards to provide a formal procedure which includes derivation of water-effect ratios, appropriate definition of sites, and enforceable monitoring provisions to assure that designated uses are protected. Both this procedure and the resulting criteria would be subject to full public participation requirements. EPA would review and approve/disapprove this protocol as a revised standard as part of the State's triennial review/revision. After adoption of the procedure, public review of a site-specific criterion could be accomplished in conjunction with the public review required for permit issuance. For public information, EPA recommends that once a year the State publish a list of site-specific criteria.

An exception to this policy applies to the waters of the jurisdictions included in the National Toxics Rule. The EPA review is not required for the jurisdictions included in the National Toxics Rule where EPA established the procedure for the State for application to the criteria promulgated. The National Toxics Rule was a formal rulemaking process (with notice and comment) in which EPA pre-authorized the use of a correctly applied water-effect ratio. That same process has not yet taken place in States not included in the National Toxics Rule.

However, the National Toxics Rule does not affect State authority to establish scientifically defensible procedures to determine Federally authorized WERs, to certify those WERs in NPDES permit proceedings, or to deny their application based on the State's risk management analysis.

As described in Section 131.36(b)(iii) of the water quality standards regulation (the official regulatory reference to the National Toxics Rule), the water-effect ratio is a site-specific calculation. As indicated on page 60866 of the preamble to the National Toxics Rule, the rule was constructed as a rebuttable presumption. The water-effect ratio is assigned a value of 1.0 until a different water-effect ratio is derived from suitable tests representative of conditions in the affected waterbody. It is the responsibility of the State to determine whether to rebut the assumed value of 1.0 in the National Toxics Rule and apply another value of the water-effect ratio in order to establish a site-specific criterion. The site-specific criterion is then used to develop appropriate NPDES permit limits. The rule thus provides a State with the flexibility to derive an appropriate site-specific criterion for specific waterbodies.

As a point of emphasis, although a water-effect ratio affects permit limits for individual dischargers, it is the State in all cases that determines if derivation of a site-specific criterion based on the water-effect ratio is allowed and it is the State that ensures that the calculations and data analysis are done completely and correctly.

3.7.6 The Resident Species Procedure

The resident Species Procedure for the derivation of a site-specific criterion accounts for differences in resident species sensitivity and differences in biological availability and/or toxicity of a material due to variability in physical and chemical characteristics of a site water. Derivation of the site-specific criterion maximum concentration (CMC) and site-specific criterion continuous concentration (CCC) are accomplished after the complete acute toxicity minimum data set requirements have been met by conducting tests with resident species in site water. Chronic tests may also be necessary. This procedure is designed to compensate concurrently for any real differences between the sensitivity range of species represented in the national data set and for site water which may markedly affect the biological availability and/or toxicity of the material of interest.

Certain families of organisms have been specified in the National Guidelines acute toxicity minimum data set (e.g., Salmonidae in fresh water and Penaeidae or Mysidae in salt water); if this or any other requirement cannot be met because the family or other group (e.g., insect or benthic crustacean) in fresh water is not represented by resident species, select a substitute(s) from a sensitive family represented by one or more resident species and meet the 8 family minimum data set requirement. If all the families at the site have been tested and the minimum data set requirements have not been met, use the most sensitive resident family mean acute value as the site-specific Final Acute Value.

To derive the criterion maximum concentration divide the site-specific Final Acute Value by two. The site-specific Final Chronic Value can be obtained as described in the Appendix L. The lower of the site-specific Final Chronic Value (as described in the recalculation procedure - Appendix L, p. 90) and the recalculated site-specific Final Residue Value becomes the site-specific criterion continuous concentration unless plant or other data (including data obtained from the site-specific tests) indicates a lower value is appropriate. If a problem is identified, judgment should be used in establishing the site-specific criterion.

The frequency of testing (e.g., the need for seasonal testing) will be related to the variability of the physical and chemical characteristics of site water as it is expected to affect the biological availability and/or toxicity of the material of interest. As the variability increases, the frequency of testing will increase. Many of the limitations discussed for the previous two procedures would also apply to this procedure.

Endnotes

1. Proceedings in production.

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CHAPTER 4

ANTIDEGRADATION

(40 CFR 131.12)

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High-quality waters are those whose quality exceeds that necessary to protect the section 101(a)(2) goals of the Act, regardless of use designation. All parameters do not need to be better quality than the State's ambient criteria for the water to be deemed a "high-quality water." EPA believes that it is best to apply antidegradation on a parameter-by-parameter basis. Otherwise, there is potential for a large number of waters not to receive antidegradation protection, which is important to attaining the goals of the Clean Water Act to restore and maintain the integrity of the Nation's waters. However, if a State has an official interpretation that differs from this interpretation, EPA will evaluate the State interpretation for conformance with the statutory and regulatory intent of the antidegradation policy. EPA has accepted approaches that do not use a strict pollutant-by-pollutant basis (USEPA, 1989c).

In "high-quality waters," under 131.12(a)(2), before any lowering of water quality occurs, there must be an antidegradation review consisting of:

- a finding that it is necessary to accommodate important economical or social development in the area in which the waters are located (this phrase is intended to convey a general concept regarding what level of social and economic development could be used to justify a change in high-quality waters);

- full satisfaction of all intergovernmental coordination and public participation provisions (the intent here is to ensure that no activity that will cause water quality to decline in existing high-quality waters is undertaken without adequate public review and intergovernmental coordination); and

- assurance that the highest statutory and regulatory requirements for point sources, including new source performance standards, and best management practices for nonpoint source pollutant controls are achieved (this requirement ensures that the limited provision for lowering water quality of high-quality waters down to "fishable/swimmable" levels will not be used to undercut the Clean Water Act requirements for point source and nonpoint source pollution control; furthermore, by ensuring compliance with such statutory and regulatory controls, there is less chance that a lowering of water quality will be sought to accommodate new economic and social development).

In addition, water quality may not be lowered to less than the level necessary to fully protect the "fishable/swimmable" uses and other existing uses. This provision is intended to provide relief only in a few extraordinary circumstances where the economic and social need for the activity clearly outweighs the benefit of maintaining water quality above that required for "fishable/swimmable" water, and both cannot be achieved. The burden of demonstration on the individual proposing such activity will be very high. In any case, moreover, the existing use must be maintained and the activity shall not preclude the maintenance of a "fishable/swimmable" level of water quality protection.

The antidegradation review requirements of this provision of the antidegradation policy are triggered by any action that would result in the lowering of water quality in a high-quality water. Such activities as new discharges or expansion of existing facilities would presumably lower water quality and would not be permissible unless the State conducts a review consistent with the previous paragraph. In addition, no permit may be issued, without an antidegradation review, to a discharger to high-quality waters with effluent limits greater than actual current loadings if such loadings will cause a lowering of water quality (USEPA, 1989c).

Antidegradation is not a "no growth" rule and was never designed or intended to be such. It is a policy that allows public decisions to be made on important environmental actions. Where the State intends to provide for development, it may decide under this section, after satisfying the requirements for intergovernmental coordination and public participation, that some lowering of water quality in "high-quality waters" is necessary to accommodate important economic or social development. Any such lower water quality must protect existing uses fully, and the State must assure that the highest statutory and regulatory requirement for all new and existing point sources and all cost-effective and reasonable BMPs for nonpoint source control are being achieved on the water body.

Section 131.12(a)(2) does not REQUIRE a State to establish BMPs for nonpoint sources where such BMP requirements do not exist. We interpret Section 131.12(a)(2) as REQUIRING States to adopt an antidegradation policy that includes a provision that will assure that all cost-effective and reasonable BMPs established under State authority are implemented for nonpoint sources before the State authorizes degradation of high quality waters by point sources (see USEPA, 1994a.)

Section 131.12(a)(2) does not mandate that States establish controls on nonpoint sources. The Act leaves it to the States to determine what, if any, controls on nonpoint sources are needed to provide for attainment of State water quality standards (See CWA Section 319.) States may adopt enforceable requirements, or voluntary programs to address nonpoint source pollution. Section 40 CFR 131.12(a)(2) does not require that States adopt or implement best management practices for nonpoint sources prior to allowing point source degradation of a high quality water. However, States that have adopted nonpoint source controls must assure that such controls are properly implemented before authorization is granted to allow point source degradation of water quality.

The rationale behind the antidegradation regulatory statement regarding achievement of statutory requirements for point sources and all cost effective and reasonable BMPs for nonpoint sources is to assure that, in high quality waters, where there are existing point or nonpoint source control compliance problems, proposed new or expanded point sources are not allowed to contribute additional pollutants that could result in degradation. Where such compliance problems exist, it would be inconsistent with the philosophy of the antidegradation policy to authorize the discharge of additional pollutants in the absence of adequate assurance that any existing compliance problems will be resolved.

EPA's regulation also requires maintenance of high quality waters except where the State finds that degradation is "necessary to accommodate important economic and social development in the area in which the waters are located." (40 CFR Part 131.12(a) (Emphasis added)). We believe this phrase should be interpreted to prohibit point source degradation as unnecessary to accommodate important economic and social development if it could be partially or completely prevented through implementation of existing State-required BMPs.

EPA believes that its antidegradation policy should be interpreted on a pollutant-by-pollutant and waterbody-by-waterbody basis. For example, degradation of a high quality waterbody by a proposed new BOD source prior to implementation of required BMPs on the same waterbody that are related to BOD loading should not be allowed. However, degradation by the new point source of BOD should not be barred solely on the basis that BMPs unrelated to BOD loadings, or which relate to other waterbodies, have not been implemented.

We recommend that States explain in their antidegradation polices or procedures how, and to what extent, the State will require implementation of otherwise non-enforceable (voluntary) BMPs before allowing point source degradation of high quality waters. EPA understands this recommendation exceeds the Federal requirements discussed in this guidance. For example, nonpoint source management plans being developed under section 319 of the Clean Water Act are likely to identify potential problems and certain voluntary means to correct those problems. The State should consider how these provisions will be implemented in conjunction with the water quality standards program.

4.6 Applicability of Water Quality Standards to Nonpoint Sources Versus Enforceability of Controls

The requirement in Section 131.21(a)(2) to implement existing nonpoint source controls before allowing degradation of a high quality water, is a subset of the broader issue of the applicability of water quality standards versus the enforceability of controls designed to implement standards. A discussion of the broader issue is included here with the intent of further clarifying the nonpoint source antidegradation question. In the following discussion, the central message is that water quality standards apply broadly and it is inappropriate to exempt whole classes of activities from standards and thereby invalidate that broader, intended purpose of adopted State water quality standards.

Water quality standards serve the dual function of establishing water quality goals for a specific waterbody and providing the basis for regulatory controls. Water quality standards apply to both point and nonpoint sources. There is a direct Federal implementation mechanism to regulate point sources of pollution but no parallel Federal regulatory process for nonpoint sources. Under State law, however, States can and do adopt mandatory nonpoint source controls.

State water quality standards play the central role in a State's water quality management program, which identifies the overall mechanism States use to integrate the various Clean Water Act water quality control elements into a coherent management framework. This includes, for example: (1) setting and revising water quality standards for all surface waterbodies, (2) monitoring water quality to provide information upon which water quality-based decisions will be made, progress evaluated, and success measured, (3) preparing a water quality inventory report under section 305(b) which documents the status of the States's water quality, (4) developing a water quality management plan which lists the standards, and prescribes the regulatory and construction activities necessary to meet the standards, (5) calculating total maximum daily loads and wasteload allocations for point sources of pollution and load allocations for nonpoint sources of pollution in the implementation of standards,(6) implementing the section 319 management plan which outlines the State's control strategy for nonpoint sources of pollution, and (7) developing permits under Section 402.

Water quality standards describe the desired condition of the aquatic environment, and, as such, reflect any activity that affects water quality. Water quality standards have broad application and use in evaluating potential impacts of water quality from a broad range of causes and sources and are not limited to evaluation of effects caused by the discharge of pollutants from point sources. In this regard, States should have in place methods by which the State can determine whether or not their standards have been achieved (including uses, criteria, and implementation of an antidegradation policy). Evaluating attainment of standards is basic to successful application of a State's water quality standards program. In the broad application of standards, these evaluations are not limited to those activities which are directly controlled through a mandatory process. Rather, these evaluations are an important component of a State's water quality management program regardless of whether or not an enforcement procedure is in place for the activity under review.

Water quality standards are implemented through State or EPA-issued water quality-based permits and through State nonpoint source control programs. Water quality standards are implemented through enforceable NPDES permits for point sources and through the installation and maintenance of BMPs for nonpoint sources. Water quality standards usually are not considered self-enforcing except where they are established as enforceable under State law. Application of water quality standards in the overall context of a water quality management program, however, is not limited to activities for which there are enforceable implementation mechanisms.

In simple terms, applicability and enforceability are two distinctly separate functions in the water quality standards program. Water quality standards are applicable to all waters and in all situations, regardless of activity or source of degradation. Implementation of those standards may not be possible in all circumstances; in such cases, the use attainability analysis may be employed. In describing the desired condition of the environment, standards establish a benchmark against which all activities which might affect that desired condition are, at a minimum, evaluated. Standards serve as the basis for water quality monitoring and there is value in identifying the source and cause of a exceedance even if, at present, those sources of impact are not regulated otherwise controlled.

It is acceptable for a State to specify particular classes of activities for which no control requirements have been established in State law. It is not acceptable, however, to specify that standards do not apply to particular classes of activities (e.g. for purposes of monitoring and assessment). To do so would abrogate one of the primary functions of water quality standards.

4.7 Outstanding National Resource Waters (ONRW) - 40 CFR 131.12(a)(3)

Outstanding National Resource Waters (ONRWs) are provided the highest level of protection under the antidegradation policy. The policy provides for protection of water quality in high-quality waters that constitute an ONRW by prohibiting the lowering of water quality. ONRWs are often regarded as highest quality waters of the United States: That is clearly the thrust of 131.12(a)(3). However, ONRW designation also offers special protection for waters of "exceptional ecological significance." These are water bodies that are important, unique, or sensitive ecologically, but whose water quality, as measured by the traditional parameters such as dissolved oxygen or pH, may not be particularly high or whose characteristics cannot be adequately described by these parameters (such as wetlands).

The regulation requires water quality to be maintained and protected in ONRWs. EPA interprets this provision to mean no new or increased discharges to ONRWs and no new or increased discharge to tributaries to ONRWs that would result in lower water quality in the ONRWs. The only exception to this prohibition, as discussed in the preamble to the Water Quality Standards Regulation (48 F.R. 51402), permits States to allow some limited activities that result in temporary and short-term changes in the water quality of ONRW. Such activities must not permanently degrade water quality or result in water quality lower than that necessary to protect the existing uses in the ONRW. It is difficult to give an exact definition of "temporary" and "short-term" because of the variety of activities that might be considered. However, in rather broad terms, EPA's view of temporary is weeks and months, not years. The intent of EPA's provision clearly is to limit water quality degradation to the shortest possible time. If a construction activity is involved, for example, temporary is defined as the length of time necessary to construct the facility and make it operational. During any period of time when, after opportunity for public participation in the decision, the State allows temporary degradation, all practical means of minimizing such degradation shall be implemented. Examples of situations in which flexibility is appropriate are listed in Exhibit 4-1.

4.8 Antidegradation Application and Implementation

Any one or a combination of several activities may trigger the antidegradation policy analysis. Such activities include a scheduled water quality standards review, the establishment of new or revised load allocations, waste load allocations, total maximum daily loads, issuance of NPDES permits, and the demonstration of need for

Example 1 ***A national park wishes to replace a defective septic tank-drainfield system in a campground. The campground is located immediately adjacent to a small stream with the ONRW use designation.***

Under the regulation, the construction could occur if best management practices were scrupulously followed to minimize any disturbance of water quality or aquatic habitat.

Example 2 ***Same situation except the campground is served by a small sewage treatment plant already discharging to the ONRW. It is desired to enlarge the treatment system and provide higher levels of treatment.***

Under the regulation, this water-quality-enhancing action would be permitted if there was only temporary increase in sediment and, perhaps, in organic loading, which would occur during the actual construction phase.

Example 3 ***A National forest with a mature, second growth of trees which are suitable for harvesting, with associated road repair and re-stabilization. Streams in the area are designated as ONRW and support trout fishing.***

The regulation intends that best management practices for timber harvesting be followed and might include preventive measures more stringent than for similar logging in less environmentally sensitive areas. Of course, if the lands were being considered for designation as wilderness areas or other similar designations, EPA's regulation should not be construed as encouraging or condoning timbering operations. The regulation allows only temporary and short-term water quality degradation while maintaining existing uses or new uses consistent with the purpose of the management of the ONRW area.

Other examples of these types of activities include maintenance and/or repair of existing boat ramps or boat docks, restoration of existing sea walls, repair of existing stormwater pipes, and replacement or repair of existing bridges.

Exhibit 4-1. Examples of Allowable Temporary Lowering of Water Quality in Outstanding National Resource Waters

advanced treatment or request by private or public agencies or individuals for a special study of the water body.

Nonpoint source activities are not exempt from the provisions of the antidegradation policy. The language of section 131.12 (a)(2) of the regulation: "Further, the State shall assure that there shall be achieved the highest statutory and regulatory requirements for all new and existing point sources and all cost-effective and reasonable best management practices for nonpoint source control . . . " reflects statutory provisions of the Clean Water Act. While it is true that the Act does not establish a federally enforceable program for nonpoint sources, it clearly intends that the BMPs developed and approved under sections 205(j), 208, 303(e), and 319 be aggressively implemented by the States.

4.8.1 Antidegradation, Load Allocation, Waste Load Allocation, Total Maximum Daily Load, and Permits

In developing or revising a load allocation (LA), waste load allocation (WLA), or total maximum daily load (TMDL) to reflect new information or to provide for seasonal variation, the antidegradation policy, as an integral part of the State water quality standards, must be applied as discussed in this section.

The TMDL/WLA/LA process distributes the allowable pollutant loadings to a water body. Such allocations also consider the contribution to pollutant loadings from nonpoint sources. This process must reflect applicable State water quality standards including the antidegradation policy. No waste load allocation can be developed or NPDES permit issued that would result in standards being violated. With respect to antidegradation, that means existing uses must be protected, water quality may not be lowered in ONRWs, and in the case of waters whose quality exceeds that necessary for the section 101(a)(2) goals of the Act, an activity cannot result in a lowering of water quality unless the applicable public participation, intergovernmental review, and baseline control requirements of the antidegradation policy have been met. Once the LA, WLA, or TMDL revision is completed, the resulting permits must incorporate discharge limitations based on this revision.

When a pollutant discharge ceases for any reason, the waste load allocations for the other dischargers in the area may be adjusted to reflect the additional loading available consistent with the antidegradation policy under two circumstances:

- In "high-quality waters" where after the full satisfaction of all public participation and intergovernmental review requirements, such adjustments are considered necessary to accommodate important economic or social development, and the "threshold" level requirements (required point and nonpoint source controls) are met.

- In less than "high-quality waters," when the expected improvement in water quality (from the ceased discharge) would not cause a better use to be achieved.

The adjusted loads still must meet water quality standards, and the new waste load allocations must be at least as stringent as technology-based limitations. Of course, all applicable requirements of the section 402 NPDES permit regulations would have to be satisfied before a permittee could increase its discharge.

If a permit is being renewed, reissued or modified to include less stringent limitations based on the revised LA/WLA/TMDL, the same antidegradation analysis applied during the LA/WLA/TMDL stage would apply during the permitting stage. It would be reasonable to allow the showing made during the LA/WLA/TMDL stage to satisfy the antidegradation showing at the permit stage. Any restrictions to less stringent limits based on antibacksliding would also apply.

If a State issues an NPDES permit that violates the required antidegradation policy, it would be subject to a discretionary EPA veto under section

402(d) or to a citizen challenge. In addition to actions on permits, any waste load allocations and total maximum daily loads violating the antidegradation policy are subject to EPA disapproval and EPA promulgation of a new waste load allocation/total maximum daily load under section 303(d) of the Act. If a significant pattern of violation was evident, EPA could constrain the award of grants or possibly revoke any Federal permitting capability that had been delegated to the State. Where EPA issues an NPDES permit, EPA will, consistent with its NPDES regulations, add any additional or more stringent effluent limitations required to ensure compliance with the State antidegradation policy incorporated into the State water quality standards. If a State fails to require compliance with its antidegradation policy through section 401 certification related to permits issued by other Federal agencies (e.g., a Corps of Engineers section 404 permit), EPA could comment unfavorably upon permit issuance. The public, of course, could bring pressure upon the permit issuing agency.

For example applications of antidegradation in the WLA and permitting process, see Exhibit 4-2.

4.8.2 Antidegradation and the Public Participation Process

Antidegradation, as with other water quality standards activities, requires public participation and intergovernmental coordination to be an effective tool in the water quality management process. 40 CFR 131.12(a)(2) contains explicit requirements for public participation and intergovernmental coordination when determining whether to allow lower water quality in high-quality waters. Nothing in either the water quality standards or the waste load allocation regulations requires the same degree of public participation or intergovernmental coordination for such non-high-quality waters as is required for high-quality waters. However public participation would still be provided in connection with the issuance of a NPDES permit or amendment of a 208 plan. Also, if the action that causes reconsideration of the existing waste loads (such as dischargers withdrawing from the area) will result in an improvement in water quality that makes a better use attainable, even if not up to the "fishable/swimmable" goal, then the water quality standards must be upgraded and full public review is required for any action affecting changes in standards. Although not specifically required by the standards regulation between the triennial reviews, we recommend that the State conduct a use attainability analysis to determine if water quality improvement will result in attaining higher uses than currently designated in situations where significant changes in waste loads are expected.

The antidegradation public participation requirement may be satisfied in several ways. The State may hold a public hearing or hearings. The State may also satisfy the requirement by providing public notice and the opportunity for the public to request a hearing. Activities that may affect several water bodies in a river basin or sub-basin may be considered in a single hearing. To ease the resource burden on both the State and public, standards issues may be combined with hearings on environmental impact statements, water management plans, or permits. However, if this is done, the public must be clearly informed that possible changes in water quality standards are being considered along with other activities. It is inconsistent with the water quality standards regulation to "back-door" changes in standards through actions on EIS's, waste load allocations, plans, or permits.

Example 1

Several facilities on a stream segment discharge phosphorus-containing wastes. Ambient phosphorus concentrations meet the designated class B (non-fishable/swimmable) standards, but barely. Three dischargers achieve elimination by developing land treatment systems. As a result, actual water quality improves (i.e., phosphorus levels decline) but not quite to the level needed to meet class A (fishable/swimmable) standards. Can the remaining dischargers now be allowed to increase their phosphorus discharge without an antidegradation analysis with the result that water quality declines (phosphorus levels increase) to previous levels?

Nothing in the water quality standards regulation explicitly prohibits this. Of course, changes in their NPDES permit limits may be subject to non-water quality constraints, such as BPT, BAT, or the NPDES antibacksliding provisions, which may restrict the increased loads.

Example 2

Suppose, in the above situation, water quality improves to the point that actual water quality now meets class A requirements. Is the answer different?

Yes. The standards must be upgraded (see section 2.8).

Example 3

As an alternative case, suppose phosphorus loadings go down and water quality improves because of a change in farming practices (e.g., initiation of a successful nonpoint source program.) Are the above answers the same?

Yes. Whether the improvement results from a change in point or nonpoint source activity is immaterial to how any aspect of the standards regulation operates. Section 131.10(d) clearly indicates that uses are deemed attainable if they can be achieved by "... cost-effective and reasonable best management practices for nonpoint source control." Section 131.12(a)(2) of the antidegradation policy contains essentially the same wording.

Exhibit 4-2. Examples of the Application of Antidegradation in the Waste Load/Load Allocation and NPDES Permitting Process

CHAPTER 7

THE WATER QUALITY-BASED APPROACH TO POLLUTION CONTROL

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7.5 Define and Allocate Control Responsibilities

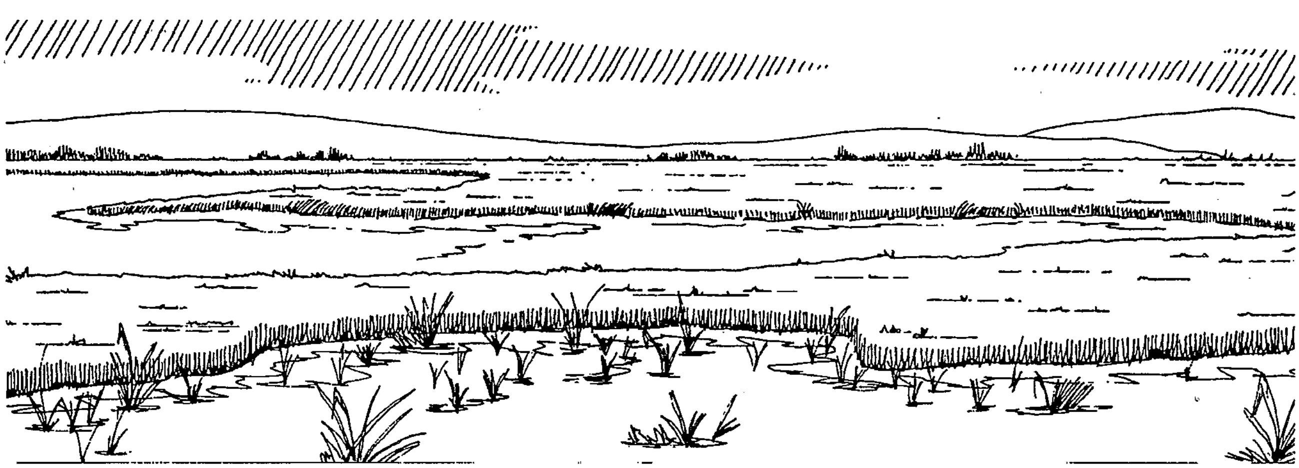
For a water quality-limited water that still requires a TMDL, a State must establish a TMDL that quantifies pollutant sources, and a margin of safety, and allocates allowable loads to the contributing point and nonpoint source discharges so that the water quality standards are attained. The development of TMDLs should be accomplished by setting priorities, considering the geographic area impacted by the pollution problem, and in some cases where there are uncertainties from lack of adequate data, using a phased approach to establishing control measures based on the TMDL.

Many water pollution concerns are areawide phenomena caused by multiple dischargers, multiple pollutants (with potential synergistic and additive effects), or nonpoint sources. Atmospheric deposition and ground water discharge may also result in significant pollutant loadings to surface waters. As a result, EPA recommends that States develop TMDLs on a watershed basis to efficiently and effectively manage the quality of surface waters.

The TMDL process is a rational method for weighing the competing pollution concerns and developing an integrated pollution reduction strategy for point and nonpoint sources. The TMDL process allows States to take a holistic view of their water quality problems from the perspective of instream conditions. Although States may define a water body to correspond with their current programs, it is expected that States will consider the extent of pollution problems and sources when defining the geographic area for developing TMDLs. In general, the geographical approach for TMDL development supports sound environmental management and efficient use of limited water quality program resources. In cases where TMDLs are developed on watershed levels, States should consider organizing permitting cycles so that all permits in a given watershed expire at the same time.

Mathematical modeling is a valuable tool for assessment of all types of water pollution problems. Dissolved oxygen depletion and nutrient enrichment from point sources are the traditional modeling problems of the past. They continue to be problems and are joined by such new challenges as nonpoint source loadings, urban stormwater runoff, toxics, and pollutants involving sediment and bioaccumulative pathways. These new pollutants and pathways require the use of new models.

All models are simplifications of reality that express our scientific understanding of the important processes. Where we don't fully understand the process(es), or cannot collect the data that would be required to set parameters in a model that would simulate the process(es), we make simplifying assumptions. All of these



simplifications increase the uncertainty of our ability to predict responses of already highly-variable systems. While the use of conservative assumptions does reduce the possibility of underestimating pollutants effects on the waterbody, the use of conservative assumptions does not reduce the uncertainty. Calibration of a model to given waterbody does more to reduce uncertainty surrounding the system's response to reduced pollutant loadings. Sensitivity analyses can further this process.

For TMDLs involving both traditional and nontraditional problems, the margins of safety can be increased and additional monitoring required to verify attainment of water quality standards, and provide data needed to recalculate the TMDL if necessary (the phased approach).

EPA regulations provide that load allocations for nonpoint sources and natural background "are best estimates of the loading which may range from reasonably accurate estimates to gross allotments . . ." (40 CFR 130.2(g)). A phased approach to developing TMDLs may be appropriate where nonpoint sources are involved and where estimates are based on limited information. Under the phased approach, TMDL includes monitoring requirements and a schedule for reassessing TMDL allocations to ensure attainment of water quality standards. Uncertainties that cannot be quantified may also exist for certain pollutants discharged primarily by point sources. In such situations a large margin of safety and follow-up monitoring are appropriate.

By pursuing the phased approach where applicable, a State can move forward to implement water quality-based control measures and adopt an explicit schedule for implementation and assessment. States can also use the phased approach to address a greater number of water bodies including threatened waters or watersheds that would otherwise not be managed. Specific requirements relating to the phased approach are discussed in *Guidance for Water Quality-based Decisions: The TMDL Process* (USEPA 1991c).

7.6 Establish Source Controls

Once a TMDL has been established for a water body (or watershed) and the appropriate source loads developed, implementation of control actions should proceed. The State or EPA is responsible for implementation, the first step being to update the water quality management plan. Next, point and nonpoint source controls should be implemented to meet waste load allocations and load allocations, respectively. Various pollution allocation schemes (i.e., determination of allowable loading from different pollution sources in the same water body) can be employed by States to optimize alternative point and nonpoint source management strategies.

The NPDES permitting process is used to limit effluent from point sources. Section 7.6.1 provides a more complete description of the NPDES process and how it fits into the water quality-based approach to permitting. Construction decisions regarding publicly owned treatment works (POTWs), including advanced treatment facilities, must also be based on the more stringent of technology-based or water quality-based limitations. These decisions should be coordinated so that the facility plan for the discharge is consistent with the limitations in the permit.

In the case of nonpoint sources, both State and local laws may authorize the implementation of nonpoint source controls such as the installation of best management practices (BMPs) or other management measures. CWA section 319 and Coastal Zone Act Reauthorization Amendments of 1990 (CZARA) section 6217 State management programs may also be utilized to implement nonpoint source control measures and practices to ensure improved water quality. Many BMPs may be implemented through section 319 programs even where State regulatory programs do not exist. In such cases, a State needs to document the coordination that may be necessary among State and local agencies, landowners, operators, and managers and then evaluate BMP implementation, maintenance, and overall effectiveness to ensure that load allocations are achieved. Section 7.6.2 discusses some of the programs associated with implementation of nonpoint source control measures.

States may also grant, condition, or deny "certification" for a federally permitted or licensed activity that may result in a discharge to the waters of the United States, if it is the State where the discharge will originate. The State decision is based on a State's determination of whether the proposed activity will comply with the requirements of certain sections of the Clean Water Act, including water quality standards under section 303. Section 7.6.3 of this Handbook contains further discussion of section 401 certification.

7.6.1 Point Source Control - the NPDES Process

Both technology-based and water quality-based controls are implemented through the National Pollutant Discharge Elimination System (NPDES) permitting process. Permit limits based on TMDLs are called water quality-based limits.

Waste load allocations establish the level of effluent quality necessary to protect water quality in the receiving water and to ensure attainment of water quality standards. Once allowable loadings have been developed through WLAs for specific pollution sources, limits are incorporated into NPDES permits. It is important to ensure that the WLA accounts for the fact that effluent quality is often highly variable. The WLA and permit limit should be calculated to prevent water quality standards impairment at all times. The reader is referred to the *Technical Support Document for Water Quality-based Toxics Control* (USEPA, 1991a) for additional information on deriving permit limits.

As a result of the 1987 Amendments to the Act, Individual Control Strategies (ICSs) were established under section 304(l)(1) for certain point source discharges of priority toxic pollutants. ICSs consist of NPDES permit limits and schedules for achieving such limits, along with documentation showing that the control measures selected are appropriate and adequate (e.g., fact sheets including information on how water quality-based limits were developed, such as total maximum daily loads and waste load allocations). Point sources with approved ICSs are to be in compliance with those ICSs as soon as possible or in no case later than 3 years from the establishment of the ICS (typically by 1992 or 1993).

When establishing WLAs for point sources in a watershed, the TMDL record should show that, in the case of any credit for future nonpoint source reductions (1) there is reasonable assurance that nonpoint source controls will be implemented and maintained, or (2) that nonpoint source reductions are demonstrated through an effective monitoring program. Assurances may include the application or utilization of local ordinances, grant conditions, or other enforcement authorities. For example, it may be appropriate to provide that a permit may be reopened when a WLA requiring more stringent limits is necessary because attainment of a nonpoint source load allocation was not demonstrated.

Some compliance implementation time may, in certain situations, be necessary and appropriate for permittees to meet new permit limits based on new standards. Under the Administrator's April 16, 1990 decision in an NPDES appeal (Star-Kist Caribe Inc., NPDES Appeal No. 88-5), the Administrator stated that the only basis in which a permittee may delay compliance after July 1, 1977 (for a post July 1977 standard), is pursuant to a schedule of compliance established in the permit which is authorized by the State in the water quality standard itself or in other State implementing regulations. Standards are made applicable to individual dischargers through NPDES permits which reflects the applicable Federal or State water quality standards. When a permit is issued, a schedule of compliance for water quality-based limitations may be included, as necessary.

7.6.2 Nonpoint Source Controls

In addition to permits for point sources, nonpoint sources controls such as management measures or best management practices (BMPs) are also to be implemented so that surface water quality objectives are met. To fully address water bodies impaired or threatened by nonpoint source pollution, States should implement their nonpoint source management programs and ensure adoption of control measures or practices by all contributors of nonpoint source pollution to the targeted watersheds.

Best management practices are the primary mechanism in section 319 of the CWA to enable achievement of water quality standards. Section 319 requires each State, in addition to developing the assessment reports discussed in section 7.2.1 of this Handbook, to adopt NPS management programs to control NPS pollution.

Sections 208(b)(2)(F) through (K) of the CWA also require States to set forth procedures and methods including land use requirements, to control to the extent feasible nonpoint sources of pollution reports.

Section 6217 of the Coastal Zone Reauthorization Amendments of 1990 (CZARA) requires that States with federally approved coastal zone management programs develop Coastal Nonpoint Pollution Control Programs to be approved by EPA and NOAA. EPA and NOAA have issued *Coastal Nonpoint Pollution Control Program; Program Development and Approval Guidance* (NOAA/EPA, 1993), which describes the program development and approval process and requirements. State programs are to employ an initial technology-based approach generally throughout the coastal management area, to be followed by a more stringent water quality-based approach to address known water quality problems. The Management Measures generally implemented throughout the coastal management area are described in *Guidance Specifying Management Measures for Sources of Nonpoint Pollution in Coastal Waters* (USEPA, 1993b).

7.6.3 CWA Section 401 Certification

States may grant, condition, or deny "certification" for a federally permitted or licensed activity that may result in a discharge to the waters of the United States, if it is the State where the discharge will originate. The language of section 401(a)(1) is very broad with respect to the activities it covers:

> [A]ny activity, including, but not limited to, the construction or operation of facilities, which <u>may</u> result in <u>any</u> <u>discharge</u> . . .

requires water quality certification.

EPA has identified five Federal permits and/or licenses that authorize activities that may result in a discharge to the waters: permits for point source discharge under section 402 and discharge of dredged and fill material under section 404 of the Clean Water Act; permits for activities in navigable waters that may affect navigation under sections 9 and 10 of the Rivers and Harbors Act (RHA); and licenses required for hydroelectric projects issued under the Federal Power Act. There are likely other Federal permits and licenses, such as permits for activities on public lands, and Nuclear Regulatory Commission licenses, which may result in a discharge and thus require 401 certification. Each State should work with EPA and the Federal agencies active in its State to determine whether 401 certification is in fact applicable.

Congress intended for the States to use the water quality certification process to ensure that no Federal license or permits would be issued that would violate State standards or become a source of pollution in the future. Also, because the States' certification of a construction permit or license also operates as certification for an operating permit (except in certain instances specified in section 401(a)(3)), it is imperative for a State review to consider all potential water quality impacts of the project, both direct and indirect, over the life of the project.

In addition, when an activity requiring 401 certification in one State (i.e. the State in which the discharge originates) will have an impact on the water quality of another State, the statute provides that after receiving notice of application from a Federal permitting or licensing agency, EPA will notify any States whose water quality may be affected. Such States have the right to submit their objections and request a hearing. EPA may also submit its evaluation and recommendations. If the use of conditions cannot ensure compliance with the affected State's water quality requirements, the Federal permitting or licensing agency shall not issue such permit or license.

The decision to grant, condition, or deny certification is based on a State's determination from data submitted by an applicant (and any other information available to the State) whether the proposed activity will comply with the requirements of certain sections of the Clean Water Act enumerated in section 401(a)(1).

These requirements address effluent limitations for conventional and nonconventional pollutants, water quality standards, new source performance standards, and toxic pollutants (sections 301, 302, 303, 306, and 307). Also included are requirements of State law or regulation more stringent than those sections or their Federal implementing regulations.

States adopt surface water quality standards pursuant to section 303 of the Clean Water Act and have broad authority to base those standards on the waters' use and value for ". . . public water supplies, propagation of fish and wildlife, recreational purposes, and . . . other purposes" (33 U.S.C. section 1313 (c)(2)(A)). All permits must include effluent limitations at least as stringent as needed to maintain established beneficial uses and to attain the quality of water designated by States for their waters. Thus, the States' water quality standards are a critical concern of the 401 certification process.

If a State grants water quality certification to an applicant for a Federal license or permit, it is in effect saying that the proposed activity <u>will</u> comply with State water quality standards (and the other CWA and State law provisions enumerated above). The State may thus deny certification because the applicant has not demonstrated that the project will comply with those requirements. Or it may place whatever limitations or conditions on the certification it determines are necessary to ensure compliance with those provisions, and with any other "appropriate" requirements of State law.

If a State denies certification, the Federal permitting or licensing agency is prohibited from issuing a permit or license. While the procedure varies from State to State, a State's decision to grant or deny certification is ordinarily subject to an administrative appeal, with review in the State courts designated for appeals of agency decisions. Court review is typically limited to the question of whether the State agency's decision is supported by the record and is not arbitrary or capricious. The courts generally presume regularity in agency procedures and defer to agency expertise in their review. (If the applicant is a Federal agency, however, at least one Federal court has ruled that the State's certification decision may be reviewed by the Federal courts.)

States may also waive water quality certification, either affirmatively or involuntarily. Under section 401(a)(1), if the State fails to act on a certification request "within a reasonable time (which shall not exceed one year)" after the receipt of an application, it forfeits its authority to grant conditionally or to deny certification.

The most important regulatory tools for the implementation of 401 certification are the States' water quality standards regulations and their 401 certification implementing regulations and guidelines. Most Tribes do not yet have water quality standards, and developing them would be a first step prior to having the authority to conduct water quality certification. Also, many States have not adopted regulations implementing their authority to grant, deny, and condition water quality certification. *Wetland and 401 Certification: Opportunities and Guidelines for States and Eligible Indian Tribes* (USEPA, 1989a) discusses specific approaches, and elements of water quality standards and 401 certification regulations that EPA views as effective to implement the States' water quality certification authority.

7.7 Monitor and Enforce Compliance

As noted throughout the previous sections, monitoring is a crucial element of water quality-based decision making. Monitoring provides data for assessing compliance with water quality-based controls and for evaluating whether the TMDL and control actions that are based on the TMDL protect water quality standards.

With point sources, dischargers are required to provide reports on compliance with NPDES permit limits. Their discharge monitoring reports (DMR) provide a key source of effluent quality data. In some instances, dischargers may also be required in the permit to assess the impact of their discharge on the receiving water. A monitoring requirement can be put into the permit as a special condition as long as the information is collected for purposes of writing a permit limit.

States should also ensure that effective monitoring programs are in place for evaluating nonpoint source control measures. EPA recognizes monitoring as a high-priority activity in a State's nonpoint source management program (55 F.R. 35262, August 28, 1990). To facilitate the implementation and evaluation of NPS controls, States should consult current guidance (USEPA, 1991g); (USEPA, 1993b). States are also encouraged to use innovative monitoring programs (e.g., rapid bioassessments (USEPA, 1989e), and volunteer monitoring (USEPA, 1990b) to provide for adequate point and nonpoint source monitoring coverage.

Dischargers are monitored to determine whether or not they are meeting their permit conditions and to ensure that expected water quality improvements are achieved. If a State has not been delegated authority for the NPDES permit program, compliance reviews of all permittees in that State are the responsibility of EPA. EPA retains oversight responsibility for State compliance programs in NPDES-delegated States. NPDES permits also contain self-monitoring requirements that are the responsibility of the individual discharger. Data obtained through self-monitoring are reported to the appropriate regulatory agency.

Based on a review of data, EPA or a State regulatory agency determines whether or not a NPDES permittee has complied with the requirements of the NPDES permit. If a facility has been identified as having apparent violations, EPA or the State will review the facility's compliance history. This review focuses on the magnitude, frequency, and duration of violations. A determination of the appropriate enforcement response is then made. EPA and States are authorized to bring civil or criminal action against facilities that violate their NPDES permits. State nonpoint source programs are enforced under State law and to the extent provided by State law.

Once control measures have been implemented, the impaired waters should be assessed to determine if water quality standards have been attained or are no longer threatened. The monitoring program used to gather the data for this assessment should be designed based on the specific pollution problems or sources. For example, it is difficult to ensure, *a priori*, that implementing nonpoint source controls will achieve expected load reductions due to inadequate selection of practices or measures, inadequate design or implementation, or lack of full participation by all contributing nonpoint sources (USEPA, 1987e). As a result, long-term monitoring efforts must be consistent over time to develop a data base adequate for analysis of control actions.

7.8 Measure Progress

If the water body achieves the applicable State water quality standards, the water body may be removed from the 303(d) list of waters still needing TMDLs. If the water quality standards are not met, the TMDL and allocations of load and waste loads must be modified. This modification should be based on the additional data and information gathered as required by the phased approach for developing a TMDL, where appropriate; as part of routine monitoring activities; and when assessing the water body for water quality standards attainment.

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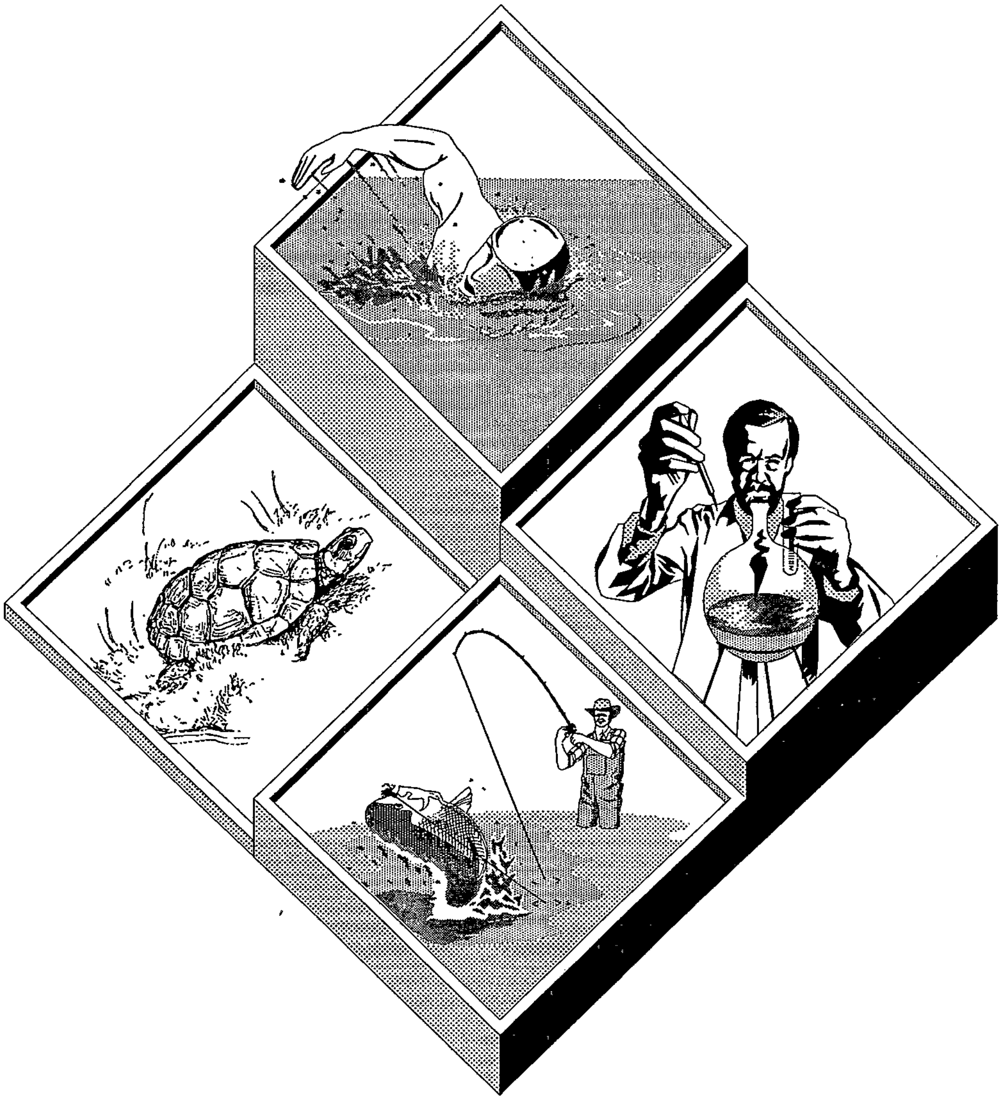
Appendixes



"... to restore and maintain the chemical, physical, and biological integrity of the Nation's waters."

Section 101(a) of the Clean Water Act

Contains update #1
August 1994

APPENDIX J

Attachments to *Office of Water Policy and Technical Guidance on Interpretation and Implementation of Aquatic Life Metals Criteria*

WATER QUALITY STANDARDS HANDBOOK

SECOND EDITION

ATTACHMENT #2

GUIDANCE DOCUMENT
ON DISSOLVED CRITERIA
Expression of Aquatic Life Criteria

October 1993

Percent Dissolved in Aquatic Toxicity Tests on Metals

The attached table contains all the data that were found concerning the percent of the total recoverable metal that was dissolved in aquatic toxicity tests. This table is intended to contain the available data that are relevant to the conversion of EPA's aquatic life criteria for metals from a total recoverable basis to a dissolved basis. (A factor of 1.0 is used to convert aquatic life criteria for metals that are expressed on the basis of the acid-soluble measurement to criteria expressed on the basis of the total recoverable measurement.) Reports by Grunwald (1992) and Brungs et al. (1992) provided references to many of the documents in which pertinent data were found. Each document was obtained and examined to determine whether it contained useful data.

"Dissolved" is defined as metal that passes through a 0.45-μm membrane filter. If otherwise acceptable, data that were obtained using 0.3-μm glass fiber filters and 0.1-μm membrane filters were used, and are identified in the table; these data did not seem to be outliers.

Data were used only if the metal was in a dissolved inorganic form when it was added to the dilution water. In addition, data were used only if they were generated in water that would have been acceptable for use as a dilution water in tests used in the derivation of water quality criteria for aquatic life; in particular, the pH had to be between 6.5 and 9.0, and the concentrations of total organic carbon (TOC) and total suspended solids (TSS) had to be below 5 mg/L. Thus most data generated using river water would not be used.

Some data were not used for other reasons. Data presented by Carroll et al. (1979) for cadmium were not used because 9 of the 36 values were above 150%. Data presented by Davies et al. (1976) for lead and Holcombe and Andrew (1978) for zinc were not used because "dissolved" was defined on the basis of polarography, rather than filtration.

Beyond this, the data were not reviewed for quality. Horowitz et al. (1992) reported that a number of aspects of the filtration procedure might affect the results. In addition, there might be concern about use of "clean techniques" and adequate QA/QC.

Each line in the table is intended to represent a separate piece of information. All of the data in the table were determined in fresh water, because no saltwater data were found. Data are becoming available for copper in salt water from the New York

Harbor study; based on the first set of tests, Hansen (1993) suggested that the average percent of the copper that is dissolved in sensitive saltwater tests is in the range of 76 to 82 percent.

A thorough investigation of the percent of total recoverable metal that is dissolved in toxicity tests might attempt to determine if the percentage is affected by test technique (static, renewal, flow-through), feeding (were the test animals fed and, if so, what food and how much), water quality characteristics (hardness, alkalinity, pH, salinity), test organisms (species, loading), etc.

The attached table also gives the freshwater criteria concentrations (CMC and CCC) because percentages for total recoverable concentrations much (e.g., more than a factor of 3) above or below the CMC and CCC are likely to be less relevant. When a criterion is expressed as a hardness equation, the range given extends from a hardness of 50 mg/L to a hardness of 200 mg/L.

The following is a summary of the available information for each metal:

Arsenic(III)

The data available indicate that the percent dissolved is about 100, but all the available data are for concentrations that are much higher than the CMC and CCC.

Cadmium

Schuytema et al. (1984) reported that "there were no real differences" between measurements of total and dissolved cadmium at concentrations of 10 to 80 ug/L (pH = 6.7 to 7.8, hardness = 25 mg/L, and alkalinity = 33 mg/L); total and dissolved concentrations were said to be "virtually equivalent".

The CMC and CCC are close together and only range from 0.66 to 8.6 ug/L. The only available data that are known to be in the range of the CMC and CCC were determined with a glass fiber filter. The percentages that are probably most relevant are 75, 92, 89, 78, and 80.

Chromium(III)

The percent dissolved decreased as the total recoverable concentration increased, even though the highest concentrations reduced the pH substantially. The percentages that are probably most relevant to the CMC are 50-75, whereas the percentages that are probably most relevant to the CCC are 86 and 61.

Chromium(VI)

The data available indicate that the percent dissolved is about 100, but all the available data are for concentrations that are much higher than the CMC and CCC.

Copper

Howarth and Sprague (1978) reported that the total and dissolved concentrations of copper were "little different" except when the total copper concentration was above 500 ug/L at hardness = 360 mg/L and pH = 8 or 9. Chakoumakos et al. (1979) found that the percent dissolved depended more on alkalinity than on hardness, pH, or the total recoverable concentration of copper.

Chapman (1993) and Lazorchak (1987) both found that the addition of daphnid food affected the percent dissolved very little, even though Chapman used yeast-trout chow-alfalfa whereas Lazorchak used algae in most tests, but yeast-trout chow-alfalfa in some tests. Chapman (1993) found a low percent dissolved with and without food, whereas Lazorchak (1987) found a high percent dissolved with and without food. All of Lazorchak's values were in high hardness water; Chapman's one value in high hardness water was much higher than his other values.

Chapman (1993) and Lazorchak (1987) both compared the effect of food on the total recoverable LC50 with the effect of food on the dissolved LC50. Both authors found that food raised both the dissolved LC50 and the total recoverable LC50 in about the same proportion, indicating that food did not raise the total recoverable LC50 by sorbing metal onto food particles; possibly the food raised both LC50s by (a) decreasing the toxicity of dissolved metal, (b) forming nontoxic dissolved complexes with the metal, or (c) reducing uptake.

The CMC and CCC are close together and only range from 6.5 to 34 ug/L. The percentages that are probably most relevant are 74, 95, 95, 73, 57, 53, 52, 64, and 91.

Lead

The data presented in Spehar et al. (1978) were from Holcombe et al. (1976). Both Chapman (1993) and Holcombe et al. (1976) found that the percent dissolved increased as the total recoverable concentration increased. It would seem reasonable to expect more precipitate at higher total recoverable concentrations and therefore a lower percent dissolved at higher concentrations. The increase in percent dissolved with increasing concentration might be due to a lowering of the pH as more metal is added if the stock solution was acidic.

The percentages that are probably most relevant to the CMC are 9, 18, 25, 10, 62, 68, 71, 75, 81, and 95, whereas the percentages that are probably most relevant to the CCC are 9 and 10.

Mercury

The only percentage that is available is 73, but it is for a concentration that is much higher than the CMC.

Nickel

The percentages that are probably most relevant to the CMC are 88, 93, 92, and 100, whereas the only percentage that is probably relevant to the CCC is 76.

Selenium

No data are available.

Silver

There is a CMC, but not a CCC. The percentage dissolved seems to be greatly reduced by the food used to feed daphnids, but not by the food used to feed fathead minnows. he percentages that are probably most relevant to the CMC are 4. 79, 79, 73, 91, 90, and 93.

Zinc

The CMC and CCC are close together and only range from 59 to 210 ug/L. The percentages that are probably most relevant are 31, 77, 77, 99, 94, 100, 103, and 96.

Recommended Values (%)[A] and Ranges of Measured Percent Dissolved Considered Most Relevant in Fresh Water

Metal	CMC		CCC	
	Recommended Value (%)	(Range %)	Recommended Value (%)	(Range %)
Arsenic(III)	95	100-104[B]	95	100-104[B]
Cadmium	85	75-92	85	75-92
Chromium(III)	85	50-75	85	61-86
Chromium(VI)	95	100[B]	95	100[B]
Copper	85	52-95	85	52-95
Lead	50	9-95	25	9-10
Mercury	35	73[B]	NA[E]	NA[E]
Nickel	85	88-100	85	76
Selenium	NA[E]	NA[C]	NA[E]	NA[C]
Silver	85	41-93	YY[D]	YY[D]
Zinc	85	31-103	85	31-103

[A] The recommended values are based on current knowledge and are subject to change as more data becomes available.

[B] All available data are for concentrations that are much higher than the CMC.

[C] NA = No data are available.

[D] YY = A CCC is not available, and therefore cannot be adjusted.

[E] NA = Bioaccumulative chemical and not appropriate to adjust to percent dissolved.

Concn.[A] (ug/L)	Percent Diss.[B]	n[C]	Species[D]	SRF[E]	Food	Hard.	Alk.	pH	Ref.
ARSENIC(III) (Freshwater: CCC = 190 ug/L; CMC = 360 ug/L)									
600-15000	104	5	?	?	?	48	41	7.6	Lima et al. 1984
12600	100	3	FM	F	No	44	43	7.4	Spehar and Fiandt 1986
CADMIUM (Freshwater: CCC = 0.66 to 2.0 ug/L; CMC = 1.8 to 8.6 ug/L)[F]									
0.16	41	?	DM	R	Yes	53	46	7.6	Chapman 1993
0.28	75	?	DM	R	Yes	103	83	7.9	Chapman 1993
0.4-4.0	92[G]	?	CS	F	No	21	19	7.1	Finlayson and Verrue 1982
13	89	3	FM	F	No	44	43	7.4	Spehar and Fiandt 1986
15-21	96	8	FM	S	No	42	31	7.5	Spehar and Carlson 1984
42	84	4	FM	S	No	45	41	7.4	Spehar and Carlson 1984
10	78	?	DM	S	No	51	38	7.5	Chapman 1993
35	77	?	DM	S	No	105	88	8.0	Chapman 1993
51	59	?	DM	S	No	209	167	8.4	Chapman 1993
6-80	80	8	?	S	No	47	44	7.5	Call et al. 1982
3-232	90[H]	5	?	F	?	46	42	7.4	Spehar et al. 1978
450-6400	70	5	FM	F	No	202	157	7.7	Pickering and Gast 1972

CHROMIUM(III) (Freshwater: CCC = 120 to 370 ug/L; CMC = 980 to 3100 ug/L)[F]

5-13	94	?	SG	F	?	25	24	7.3	Stevens and Chapman 1984
19-495	86	?	SG	F	?	25	24	7.2	Stevens and Chapman 1984
>1100	50-75	?	SG	F	No	25	24	7.0	Stevens and Chapman 1984
42	54	?	DM	R	Yes	206	166	8.2	Chapman 1993
114	61	?	DM	R	Yes	52	45	7.4	Chapman 1993
16840	26	?	DM	S	No	<51	9	6.3[I]	Chapman 1993
26267	32	?	DM	S	No	110	9	6.7	Chapman 1993
27416	27	?	DM	S	No	96	10	6.0[I]	Chapman 1993
58665	23	?	DM	S	No	190	25	6.2[I]	Chapman 1993

CHROMIUM(VI) (Freshwater: CCC = 11 ug/L; CMC = 16 ug/L)

>25,000	100	1	FM,GF	F	Yes	220	214	7.6	Adelman and Smith 1976
43,300	99.5	4	FM	F	No	44	43	7.4	Spehar and Fiandt 1986

COPPER (Freshwater: CCC = 6.5 to 21 ug/L; CMC = 9.2 to 34 ug/L)[F]

10-30	74	?	CT	F	No	27	20	7.0	Chakoumakos et al. 1979
40-200	78	?	CT	F	No	154	20	6.8	Chakoumakos et al. 1979
30-100	79	?	CT	F	No	74	23	7.6	Chakoumakos et al. 1979
100-200	82	?	CT	F	No	192	72	7.0	Chakoumakos et al. 1979
20-200	86	?	CT	F	No	31	78	8.3	Chakoumakos et al. 1979
40-300	87	?	CT	F	No	83	70	7.4	Chakoumakos et al. 1979
10-80	89	?	CT	F	No	25	169	8.5	Chakoumakos et al. 1979

300-1300	92	?	CT	F	No	195	160	7.0	Chakoumakos et al. 1979
100-400	94	?	CT	F	No	70	174	8.5	Chakoumakos et al. 1979
3-4[J]	125-167	2	CD	R	Yes	31	38	7.2	Carlson et al. 1986a,b
12-91[J]	79-84	3	CD	R	Yes	31	38	7.2	Carlson et al. 1986a,b
18-19	95	2	DA	S	No	52	55	7.7	Carlson et al. 1986b
20[J]	95	1	DA	R	No	31	38	7.2	Carlson et al. 1986b
50	96	2	FM	S	No	52	55	7.7	Carlson et al. 1986b
175[J]	91	2	FM	R	No	31	38	7.2	Carlson et al. 1986b
5-52	>82[K]	?	FM	F	Yes[L]	47	43	8.0	Lind et al. 1978
6-80	83[G]	?	CS	F	No	21	19	7.1	Finlayson and Verrue 1982
6.7	57	?	DM	S	No	49	37	7.7	Chapman 1993
35	43	?	DM	S	Yes	48	39	7.4	Chapman 1993
13	73	?	DM	R	Yes	211	169	8.1	Chapman 1993
16	57	?	DM	R	Yes	51	44	7.6	Chapman 1993
51	39	?	DM	R	Yes	104	83	7.8	Chapman 1993
32	53	?	DM	S	No	52	45	7.8	Chapman 1993
33	52	?	DM	S	No	105	79	7.9	Chapman 1993
39	64	?	DM	S	No	106	82	8.1	Chapman 1993
25-84	96	14	FM,GM	S	No	50	40	7.0	Hammermeister et al. 1983
17	91	6	DM	S	No	52	43	7.3	Hammermeister et al. 1983
120	88	14	SG	S	No	48	47	7.3	Hammermeister et al. 1983
15-90	74	19	?	S	No	48	47	7.7	Call et al. 1982
12-162	80[H]	?	BG	F	Yes[L]	45	43	7-8	Benoit 1975
28-58	85	6	DM	R	No	168	117	8.0	Lazorchak 1987
26-59	79	7	DM	R	Yes[M]	168	117	8.0	Lazorchak 1987
56,101	86	2	DM	R	Yes[N]	168	117	8.0	Lazorchak 1987

96	86	4	FM	F	No	44	43	7.4	Spehar and Fiandt 1986
160	94	1	FM	S	No	203	171	8.2	Geckler et al. 1976
230-3000	>69->79	?	CR	F	No	17	13	7.6	Rice and Harrison 1983

LEAD (Freshwater: CCC = 1.3 to 7.7 ug/L; CMC = 34 to 200 ug/L)[F]

17	9	?	DM	R	Yes	52	47	7.6	Chapman 1993
181	18	?	DM	R	Yes	102	86	7.8	Chapman 1993
193	25	?	DM	R	Yes	151	126	8.1	Chapman 1993
612	29	?	DM	S	No	50	--	---	Chapman 1993
952	33	?	DM	S	No	100	--	---	Chapman 1993
1907	~38	?	DM	S	No	150	--	---	Chapman 1993
7-29	10	?	EZ	R	No	22	--	---	JRB Associates 1983
34	62[H]	?	BT	F	Yes	44	43	7.2	Holcombe et al. 1976
58	68[H]	?	BT	F	Yes	44	43	7.2	Holcombe et al. 1976
119	71[H]	?	BT	F	Yes	44	43	7.2	Holcombe et al. 1976
235	75[H]	?	BT	F	Yes	44	43	7.2	Holcombe et al. 1976
474	81[H]	?	BT	F	Yes	44	43	7.2	Holcombe et al. 1976
4100	82[H]	?	BT	F	No	44	43	7.2	Holcombe et al. 1976
2100	79	7	FM	F	No	44	43	7.4	Spehar and Fiandt 1986
220-2700	96	14	FM,GM,DM	S	No	49	44	7.2	Hammermeister et al. 1983
580	95	14	SG	S	No	51	48	7.2	Hammermeister et al. 1983

MERCURY(II) (Freshwater: CMC = 2.4 ug/L)

172	73	1	FM	F	No	44	43	7.4	Spehar and Fiandt 1986

NICKEL (Freshwater: CCC = 88 to 280 ug/L; CMC = 790 to 2500 ug/L)[F]

21	81	?	DM	R	Yes	51	49	7.4	Chapman 1993
150	76	?	DM	R	Yes	107	87	7.8	Chapman 1993
578	87	?	DM	R	Yes	205	161	8.1	Chapman 1993
645	88	?	DM	S	No	54	43	7.7	Chapman 1993
1809	93	?	DM	S	No	51	44	7.7	Chapman 1993
1940	92	?	DM	S	No	104	84	8.2	Chapman 1993
2344	100	?	DM	S	No	100	84	7.9	Chapman 1993
4000	90	?	PK	R	No	21	--	---	JRB Associates 1983

SELENIUM (FRESHWATER: CCC = 5 ug/L; CMC = 20 ug/L)

No data are available.

SILVER (Freshwater: CMC = 1.2 to 13 ug/L; a CCC is not available)

0.19	74	?	DM	S	No	47	37	7.6	Chapman 1993
9.98	13	?	DM	S	Yes	47	37	7.5	Chapman 1993
4.0	41	?	DM	S	No	36	25	7.0	Nebeker et al. 1983
4.0	11	?	DM	S	Yes	36	25	7.0	Nebeker et al. 1983
3	79	?	FM	S	No	51	49	8.1	UWS 1993
2-54	79	?	FM	S	Yes[O]	49	49	7.9	UWS 1993
2-32	73	?	FM	S	No	50	49	8.1	UWS 1993
4-32	91	?	FM	S	No	48	49	8.1	UWS 1993
5-89	90	?	FM	S	No	120	49	8.2	UWS 1993
6-401	93	?	FM	S	No	249	49	8.1	UWS 1993

<u>ZINC</u> (Freshwater: CCC = 59 to 190 ug/L; CMC 65 to 210 ug/L)[F]

52	31	?	DM	R	Yes	211	169	8.2	Chapman 1993
62	77	?	DM	R	Yes	104	83	7.8	Chapman 1993
191	77	?	DM	R	Yes	52	47	7.5	Chapman 1993
356	74	?	DM	S	No	54	47	7.6	Chapman 1993
551	78	?	DM	S	No	105	85	8.1	Chapman 1993
741	76	?	DM	S	No	196	153	8.2	Chapman 1993
7[J]	71-129	2	CD	R	Yes	31	38	7.2	Carlson et al. 1986b
18-273[J]	81-107	2	CD	R	Yes	31	38	7.2	Carlson et al. 1986b
167[J]	99	2	CD	R	No	31	38	7.2	Carlson et al. 1986b
180	94	1	CD	S	No	52	55	7.7	Carlson et al. 1986b
188-393[J]	100	2	FM	R	No	31	38	7.2	Carlson et al. 1986b
551	100	1	FM	S	No	52	55	7.7	Carlson et al. 1986b
40-500	95[G]	?	CS	F	No	21	19	7.1	Finlayson and Verrue 1982
1940	100	?	AS	F	No	20	12	7.1	Sprague 1964
5520	83	?	AS	F	No	20	12	7.9	Sprague 1964
<4000	90	?	FM	F	No	204	162	7.7	Mount 1966
>4000	70	?	FM	F	No	204	162	7.7	Mount 1966
160-400	103	13	FM,GM,DM	S	No	52	43	7.5	Hammermeister et al. 1983
240	96	13	SG	S	No	49	46	7.2	Hammermeister et al. 1983

[A] Total recoverable concentration.

[B] Except as noted, a 0.45-μm membrane filter was used.

[c] Number of paired comparisons.

[D] The abbreviations used are:

AS = Atlantic salmon	DM = *Daphnia magna*
BT = Brook trout	EZ = *Elassoma zonatum*
CD = *Ceriodaphnia dubia*	FM = Fathead minnow
CR = Crayfish	GF = Goldfish
CS = Chinook salmon	GM = Gammarid
CT = Cutthroat trout	PK = *Palaemonetes kadiakensis*
DA = Daphnids	SG = *Salmo gairdneri*

[E] The abbreviations used are:
- S = static
- R = renewal
- F = flow-through

[F] The two numbers are for hardnesses of 50 and 200 mg/L, respectively.

[G] A 0.3-μm glass fiber filter was used.

[H] A 0.10-μm membrane filter was used.

[I] The pH was below 6.5.

[J] The dilution water was a clean river water with TSS and TOC below 5 mg/L.

[K] Only limited information is available concerning this value.

[L] It is assumed that the solution that was filtered was from the test chambers that contained fish and food.

[M] The food was algae.

[N] The food was yeast-trout chow-alfalfa.

[O] The food was frozen adult brine shrimp.

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ATTACHMENT #3

GUIDANCE DOCUMENT
ON DYNAMIC MODELING AND TRANSLATORS
August 1993

Total Maximum Daily Loads (TMDLs) and Permits

o Dynamic Water Quality Modeling

Although not specifically part of the reassessment of water quality criteria for metals, dynamic or probabilistic models are another useful tool for implementing water quality criteria, especially those for protecting aquatic life. Dynamic models make best use of the specified magnitude, duration, and frequency of water quality criteria and thereby provide a more accurate calculation of discharge impacts on ambient water quality. In contrast, steady-state modeling is based on various simplifying assumptions which makes it less complex and less accurate than dynamic modeling. Building on accepted practices in water resource engineering, ten years ago OW devised methods allowing the use of probability distributions in place of worst-case conditions. The description of these models and their advantages and disadvantages is found in the 1991 Technical Support Document for Water Quality-based Toxic Control (TSD).

Dynamic models have received increased attention in the last few years as a result of the perception that static modeling is over-conservative due to environmentally conservative dilution assumptions. This has led to the misconception that dynamic models will always justify less stringent regulatory controls (e.g. NPDES effluent limits) than static models. In effluent dominated waters where the upstream concentrations are relatively constant, however, a dynamic model will calculate a more stringent wasteload allocation than will a steady state model. The reason is that the critical low flow required by many State water quality standards in effluent dominated streams occurs more frequently than once every three years. When other environmental factors (e.g. upstream pollutant concentrations) do not vary appreciably, then the overall return frequency of the steady state model may be greater than once in three years. A dynamic modeling approach, on the other hand, would be more stringent, allowing only a once in three year return frequency. As a result, EPA considers dynamic models to be a more accurate rather than a less stringent approach to implementing water quality criteria.

The 1991 TSD provides recommendations on the use of steady state and dynamic water quality models. The reliability of any modeling technique greatly depends on the accuracy of the data used in the analysis. Therefore, the selection of a model also depends upon the data. EPA recommends that steady state wasteload allocation analyses generally be used where few or no whole effluent toxicity or specific chemical measurements are available, or where daily receiving water flow records are not available. Also, if staff resources are insufficient to use and defend the use of dynamic models, then steady state models may be necessary. If adequate receiving water flow and effluent concentration data are available to estimate frequency distributions, EPA recommends that one of the dynamic wasteload allocation modeling techniques be used to derive wasteload allocations which will more exactly maintain water quality standards. The minimum data required for input into dynamic models include at least 30 years of river flow data and one year of effluent and ambient pollutant concentrations.

- o Dissolved-Total Metal Translators

When water quality criteria are expressed as the dissolved form of a metal, there is a need to translate TMDLs and NPDES permits to and from the dissolved form of a metal to the total recoverable form. TMDLs for toxic metals must be able to calculate 1) the dissolved metal concentration in order to ascertain attainment of water quality standards and 2) the total recoverable metal concentration in order to achieve mass balance. In meeting these requirements, TMDLs consider metals to be conservative pollutants and quantified as total recoverable to preserve conservation of mass. The TMDL calculates the dissolved or ionic species of the metals based on factors such as total suspended solids (TSS) and ambient pH. (These assumptions ignore the complicating factors of metals interactions with other metals.) In addition, this approach assumes that ambient factors influencing metal partitioning remain constant with distance down the river. This assumption probably is valid under the low flow conditions typically used as design flows for permitting of metals (e.g., 7Q10, 4B3, etc) because erosion, resuspension, and wet weather loadings are unlikely to be significant and river chemistry is generally stable. In steady-state dilution modeling, metals releases may be assumed to remain fairly constant (concentrations exhibit low variability) with time.

EPA's NPDES regulations require that metals limits in permits be stated as total recoverable in most cases (see 40 CFR §122.45(c)). Exceptions occur when an effluent guideline specifies the limitation in another form of the metal or the approved analytical methods measure only the dissolved form. Also, the permit writer may express a metals limit in another form (e.g., dissolved, valent, or total) when required, in highly unusual cases, to carry out the provisions of the CWA.

The preamble to the September 1984 National Pollutant Discharge Elimination System Permit Regulations states that the total recoverable method measures dissolved metals plus that portion of solid metals that can easily dissolve under ambient conditions (see 49 Federal Register 38028, September 26, 1984). This method is intended to measure metals in the effluent that are or may easily become environmentally active, while not measuring metals that are expected to settle out and remain inert.

The preamble cites, as an example, effluent from an electroplating facility that adds lime and uses clarifiers. This effluent will be a combination of solids not removed by the clarifiers and residual dissolved metals. When the effluent from the clarifiers, usually with a high pH level, mixes with receiving water having significantly lower pH level, these solids instantly dissolve. Measuring dissolved metals in the effluent, in this case, would underestimate the impact on the receiving water. Measuring with the total metals method, on the other hand, would measure metals that would be expected to disperse or settle out and remain inert or be covered over. Thus, measuring total recoverable metals in the effluent best approximates the amount of metal likely to produce water quality impacts.

However, the NPDES rule does not require in any way that State water quality standards be in the total recoverable form; rather, the rule requires permit writers to consider the translation between differing metal forms in the calculation of the permit limit so that a total recoverable limit can be established. Therefore, both the TMDL and NPDES uses of water quality criteria require the ability to translate from the dissolved form and the total recoverable form.

Many toxic substances, including metals, have a tendency to leave the dissolved phase and attach to suspended solids. The partitioning of toxics between solid and dissolved phases can be determined as a function of a pollutant-specific partition coefficient and the concentration of solids. This function is expressed by a linear partitioning equation:

$$C = \frac{C_{Tf}}{1 + K_d \cdot TSS \cdot 10^{-6}}$$

where,

C = dissolved phase metal concentration,
C_{Tf} = total metal concentration,
TSS = total suspended solids concentration, and
K_d = partition coefficient.

A key assumption of the linear partitioning equation is that the sorption reaction reaches dynamic equilibrium at the point of application of the criteria; that is, after allowing for initial mixing the partitioning of the pollutant between the adsorbed and dissolved forms can be used at any location to predict the fraction of pollutant in each respective phase.

Successful application of the linear partitioning equation relies on the selection of the partition coefficient. The use of a partition coefficient to represent the degree to which toxics adsorb to solids is most readily applied to organic pollutants; partition coefficients for metals are more difficult to define. Metals typically exhibit more complex speciation and complexation reactions than organics and the degree of partitioning can vary greatly depending upon site-specific water chemistry. Estimated partition coefficients can be determined for a number of metals, but waterbody or site-specific observations of dissolved and adsorbed concentrations are preferred.

EPA suggests three approaches for instances where a water quality criterion for a metal is expressed in the dissolved form in a State's water quality standards:

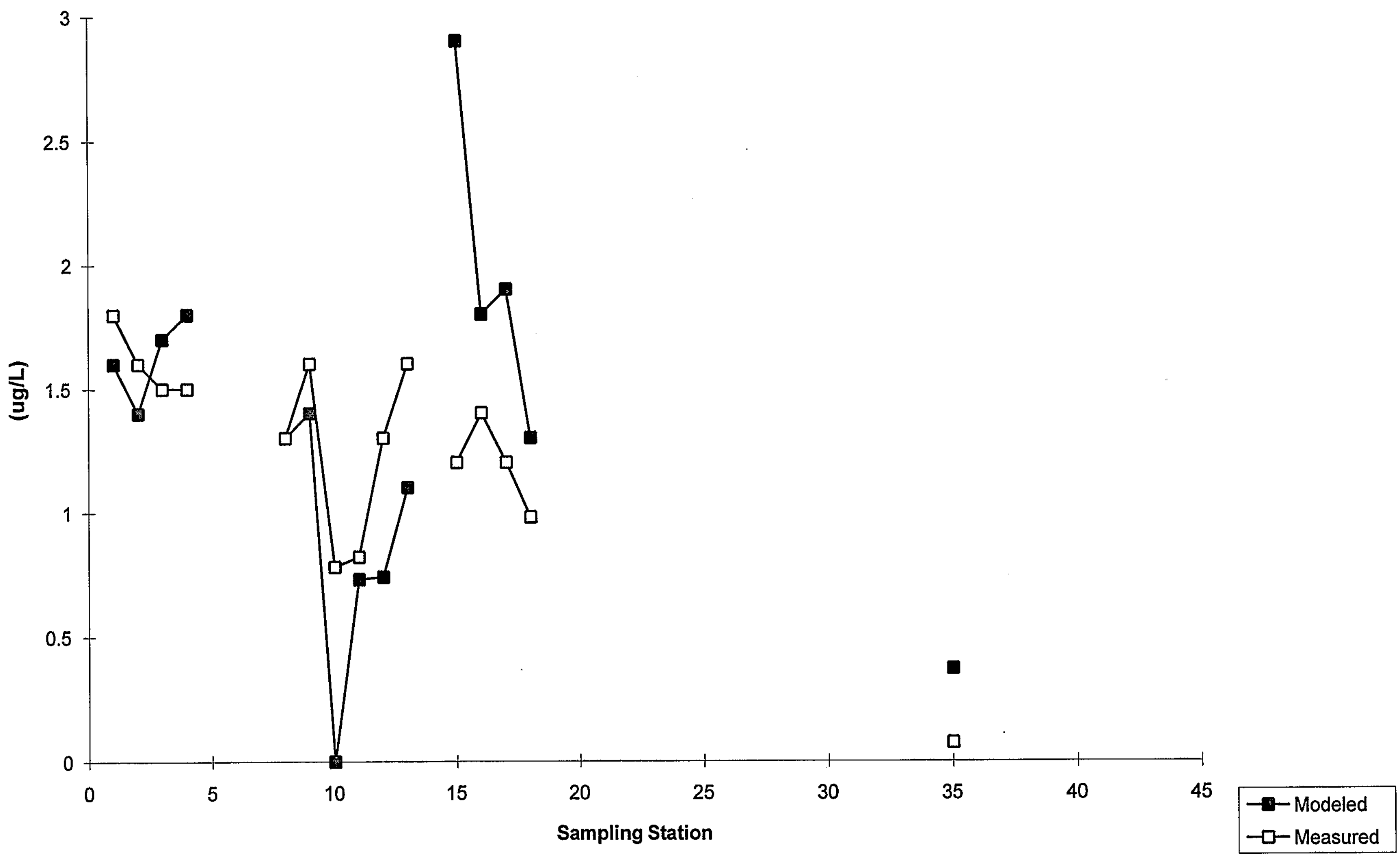
1. Using clean analytical techniques and field sampling procedures with appropriate QA/QC, collect receiving water samples and determine site specific values of K_d for each metal. Use these K_d values to "translate" between total recoverable and dissolved metals in receiving water. This approach is more difficult to apply because it relies upon the availability of good quality measurements of ambient metal concentrations. This approach provides an accurate assessment of the dissolved metal fraction providing sufficient samples are collected. EPA's initial recommendation is that at least four pairs of total recoverable and dissolved ambient metal measurements be made during low flow conditions or 20 pairs over all flow conditions. EPA suggests that the average of data collected during low flow or the 95th percentile highest dissolved fraction for all flows be used. The low flow average provides a representative picture of conditions during the rare low flow events. The 95th percentile highest dissolved fraction for all flows provides a critical condition approach analogous to the approach used to identify low flows and other critical environmental conditions.

2. Calculate the total recoverable concentration for the purpose of setting the permit limit. Use a value of 1 unless the permittee has collected data (see #1 above) to show that a different ratio should be used. The value of 1 is conservative and will not err on the side of violating standards. This approach is very simple to apply because it places the entire burden of data collection and analysis solely upon permitted facilities. In terms of technical merit, it has the same characteristics of the previous approach. However, permitting authorities may be faced with difficulties in negotiating with facilities on the amount of data necessary to determine the ratio and the necessary quality control methods to assure that the ambient data are reliable.

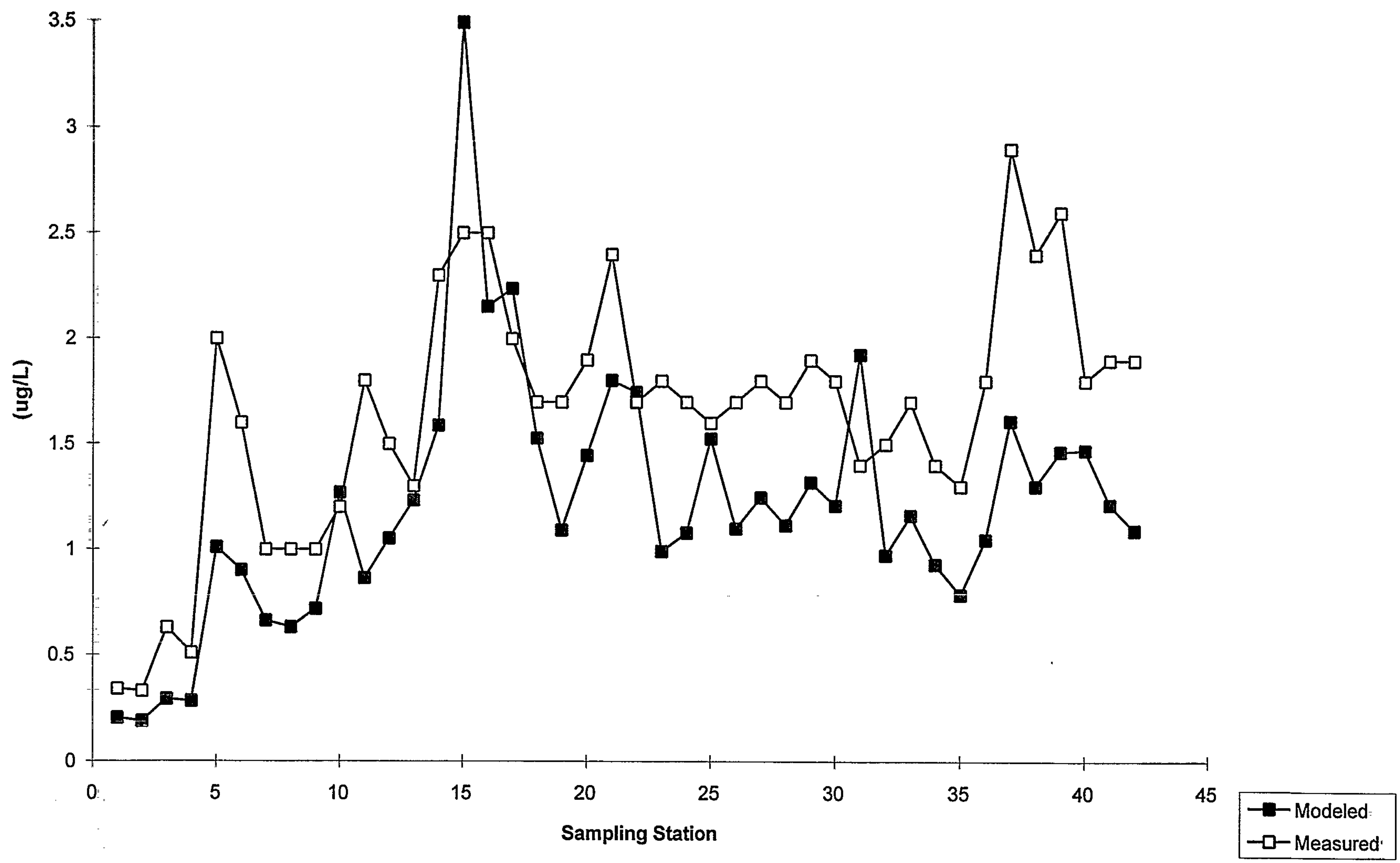
3. Use the historical data on total suspended solids (TSS) in receiving waterbodies at appropriate design flows and K_d values presented in the Technical Guidance Manual for Performing Waste Load Allocations. Book II. Streams and Rivers. EPA-440/4-84-020 (1984) to "translate" between (total recoverable) permits limits and dissolved metals in receiving water. This approach is fairly simple to apply. However, these K_d values are suspect due to possible quality assurance problems with the data used to develop the values. EPA's initial analysis of this approach and these values in one site indicates that these K_d values generally over-estimate the dissolved fraction of metals in ambient waters (see Figures following). Therefore, although this approach may not provide an accurate estimate of the dissolved fraction, the bias in the estimate is likely to be a conservative one.

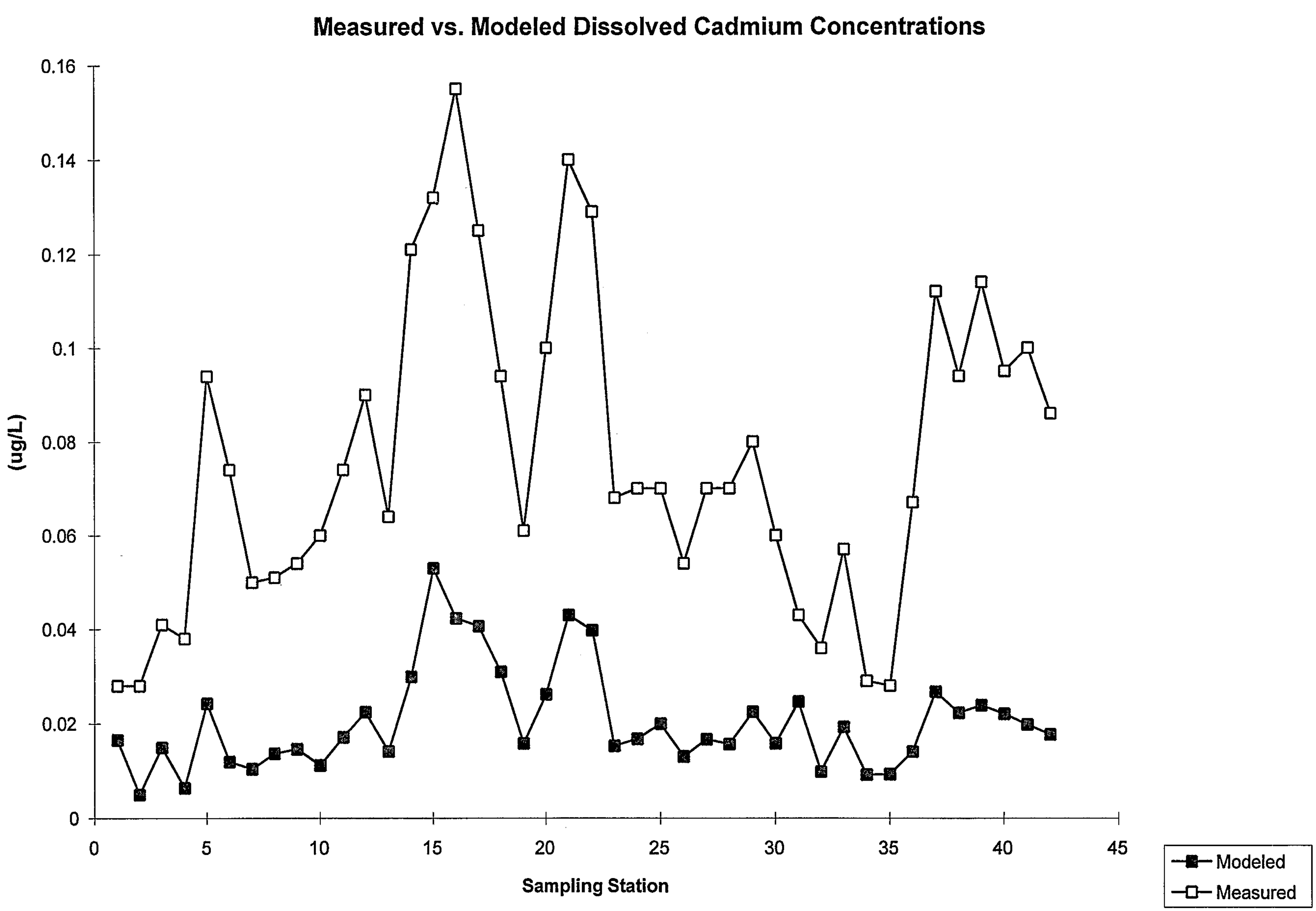
EPA suggests that regulatory authorities use approaches #1 and #2 where States express their water quality standards in the dissolved form. In those States where the standards are in the total recoverable or acid soluble form, EPA recommends that no translation be used until the time that the State changes the standards to the dissolved form. Approach #3 may be used as an interim measure until the data are collected to implement approach #1.

Measured vs. Modeled Dissolved Arsenic Concentrations



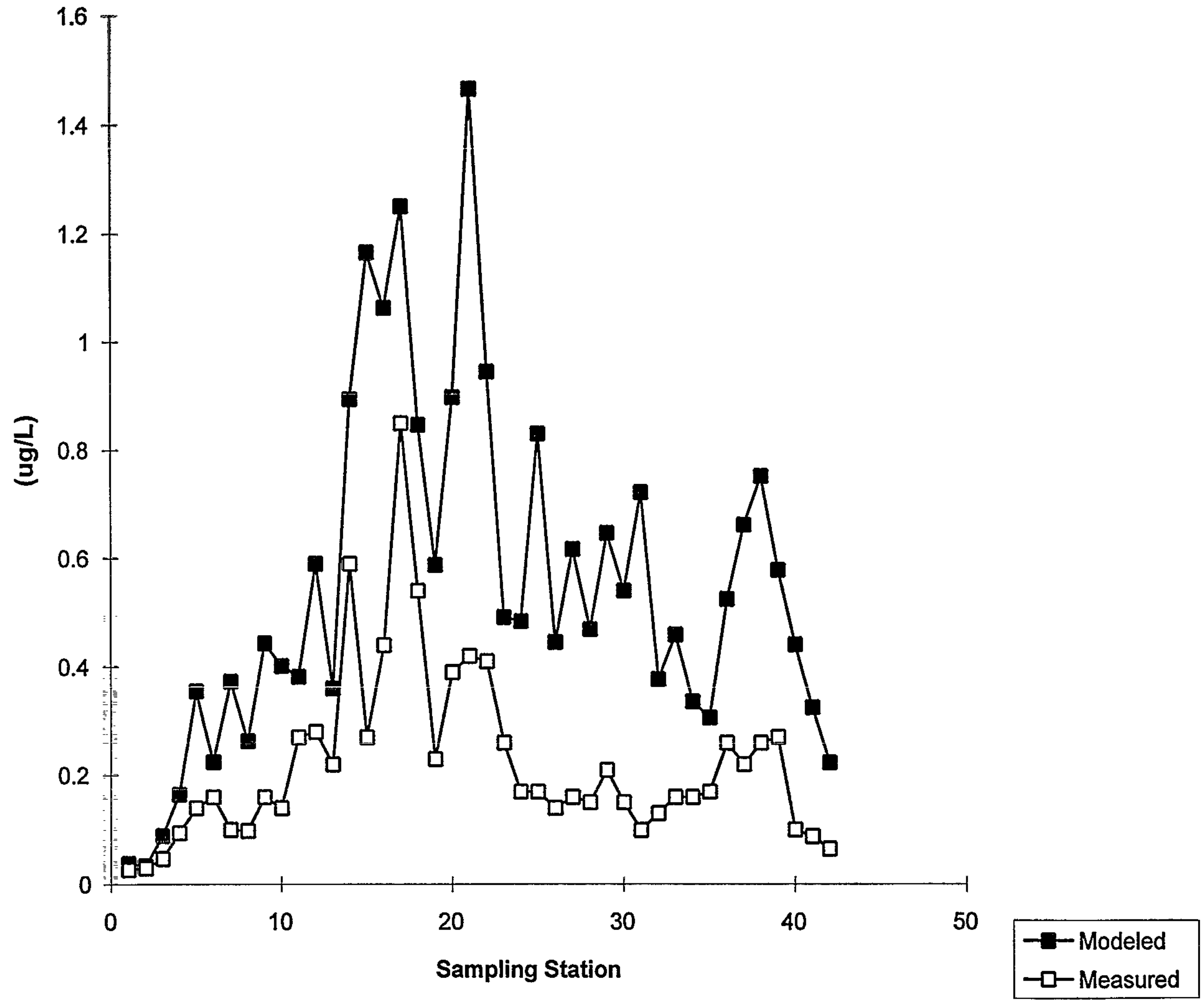
Measured vs. Modeled Dissolved Copper Concentrations



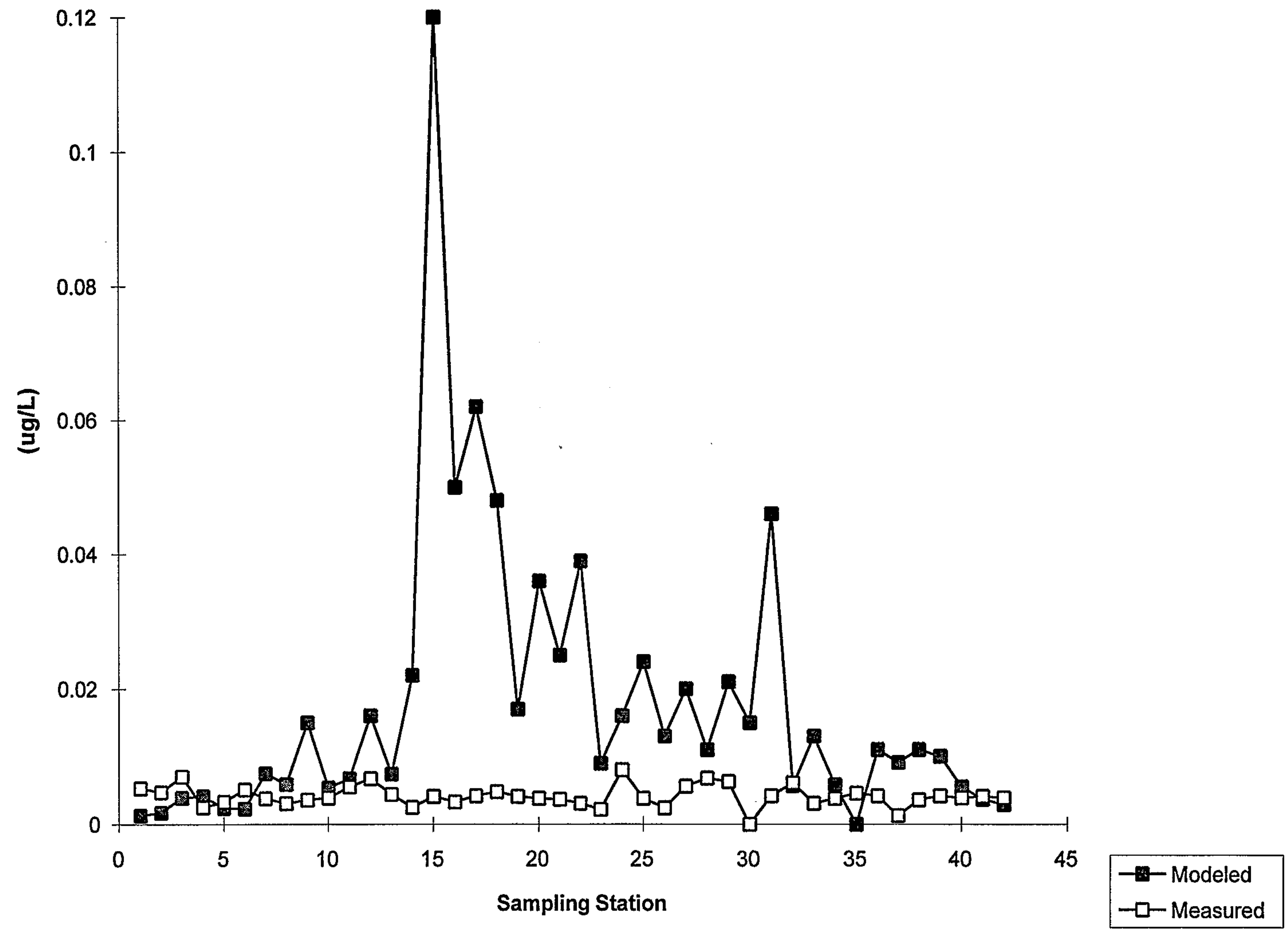


Measured vs. Modeled Dissolved Cadmium Concentrations
(ug/L)
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0
5
10
15
20
25
30
35
40
45
Sampling Station
Modeled
Measured

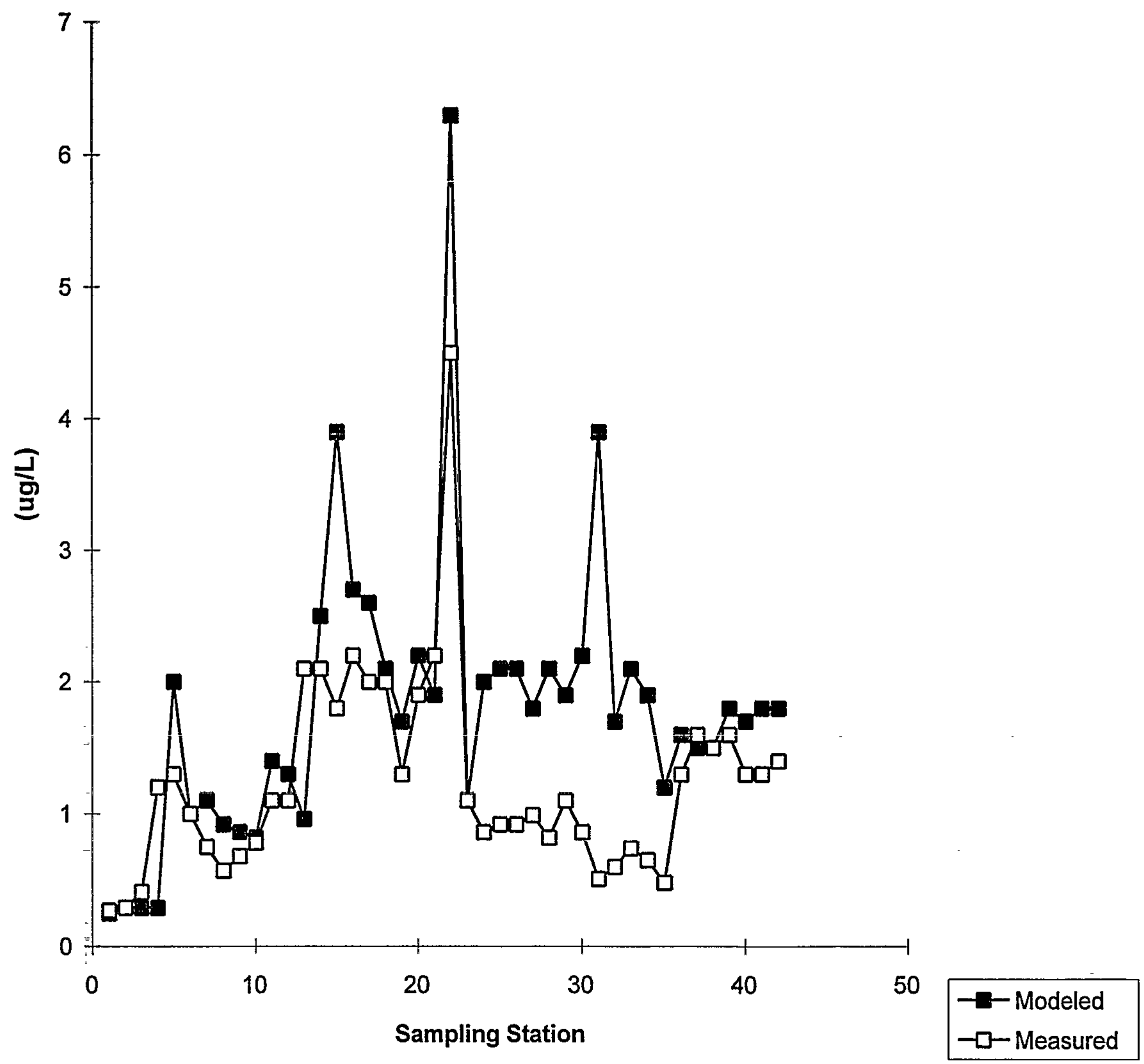
Measured vs. Modeled Dissolved Lead Concentrations



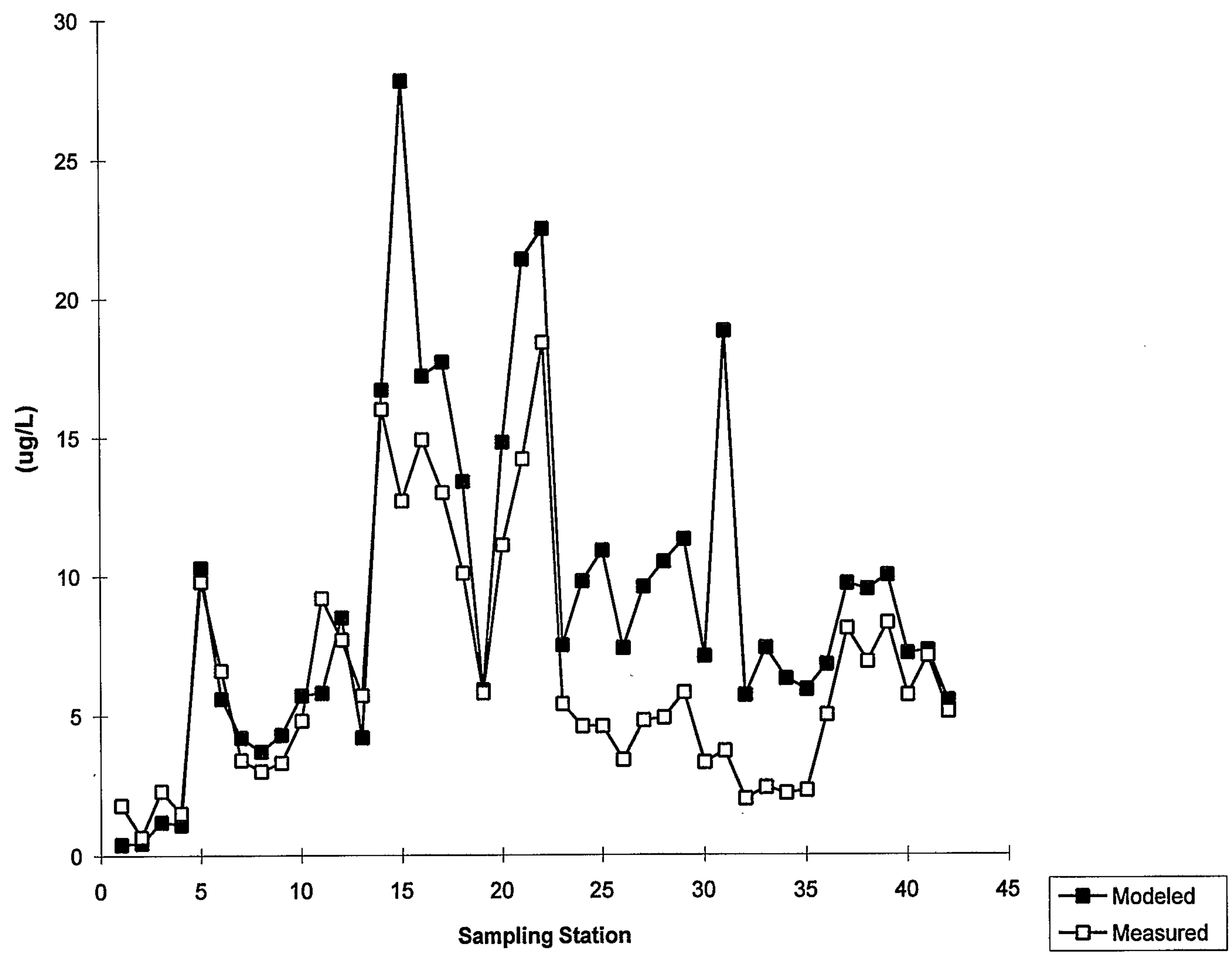
Measured vs. Modeled Dissolved Mercury Concentrations



Measured vs. Modeled Dissolved Nickel Concentrations



Measured vs. Modeled Dissolved Zinc Concentrations



ATTACHMENT #4

GUIDANCE DOCUMENT
ON CLEAN ANALYTICAL TECHNIQUES AND MONITORING

October 1993

Guidance on Monitoring

o Use of Clean Sampling and Analytical Techniques

Pages 98-108 of the WER guidance document (Appendix L of the *Water Quality Standards Handbook-Second Edition*) provides some general guidance on the use of clean techniques. The Office of Water recommends that this guidance be used by States and Regions as an interim step while the Office of Water prepares more detailed guidance.

o Use of Historical DMR Data

With respect to effluent or ambient monitoring data reported by an NPDES permittee on a Discharge Monitoring Report (DMR), the certification requirements place the burden on the permittee for collecting and reporting quality data. The certification regulation at 40 CFR 122.22(d) requires permittees, when submitting information, to state: "I certify under penalty of law that this document and all attachments were prepared under my direction or supervision in accordance with a system designed to assure that qualified personnel properly gather and evaluate the information submitted. Based on my inquiry of the person or persons who manage the system, or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations."

Permitting authorities should continue to consider the information reported in DMRs to be true, accurate, and complete as certified by the permittee. Under 40 CFR 122.41(l)(8), however, as soon as the permittee becomes aware of new information specific to the effluent discharge that calls into question the accuracy of the DMR data, the permittee must submit such information to the permitting authority. Examples of such information include a new finding that the reagents used in the laboratory analysis are contaminated with trace levels of metals, or a new study that the sampling equipment imparts trace metal contamination. This information must be specific to the discharge and based on actual measurements rather than extrapolations from reports from other facilities. Where a permittee submits information supporting the contention that the previous data are questionable and the permitting authority agrees with the findings of the information, EPA expects that permitting authorities will consider such information in determining appropriate enforcement responses.

In addition to submitting the information described above, the permittee also must develop procedures to assure the collection and analysis of quality data that are true, accurate, and complete. For example, the permittee may submit a revised quality assurance plan that describes the specific procedures to be undertaken to reduce or eliminate trace metal contamination.

APPENDIX L

Interim Guidance on Determination and Use of Water-Effect Ratios for Metals

WATER QUALITY STANDARDS HANDBOOK

SECOND EDITION

FEB 22 1994

EPA-823-B-94-001

MEMORANDUM

SUBJECT: Use of the Water-Effect Ratio in Water Quality Standards

FROM: Tudor T. Davies, Director
Office of Science and Technology

TO: Water Management Division Directors, Regions I - X
State Water Quality Standards Program Directors

PURPOSE

There are two purposes for this memorandum.

The first is to transmit the Interim Guidance on the Determination and Use of Water-Effect Ratios for Metals. EPA committed to developing this guidance to support implementation of federal standards for those States included in the National Toxics Rule.

The second is to provide policy guidance on whether a State's application of a water-effect ratio is a site-specific criterion adjustment subject to EPA review and approval/disapproval.

BACKGROUND

In the early 1980's, members of the regulated community expressed concern that EPA's laboratory-derived water quality criteria might not accurately reflect site-specific conditions because of the effects of water chemistry and the ability of species to adapt over time. In response to these concerns, EPA created three procedures to derive site-specific criteria. These procedures were published in the Water Quality Standards Handbook, 1983.

Site-specific criteria are allowed by regulation and are subject to EPA review and approval. The Federal water quality standards regulation at section 131.11(b)(1) provides States with the opportunity to adopt water quality criteria that are "...modified to reflect site-specific conditions." Under section 131.5(a)(2), EPA reviews standards to determine "whether a State has adopted criteria to protect the designated water uses."

On December 22, 1992, EPA promulgated the National Toxics Rule which established Federal water quality standards for 14 States which had not met the requirements of Clean Water Act Section 303(c)(2)(B). As part of that rule, EPA gave the States discretion to adjust the aquatic life criteria for metals to reflect site-specific conditions through use of a water-effect ratio. A water-effect ratio is a means to account for a difference between the toxicity of the metal in laboratory dilution water and its toxicity in the water at the site.

In promulgating the National Toxics Rule, EPA committed to issuing updated guidance on the derivation of water-effect ratios. The guidance reflects new information since the previous guidance and is more comprehensive in order to provide greater clarity and increased understanding. This new guidance should help standardize procedures for deriving water-effect ratios and make results more comparable and defensible.

Recently, an issue arose concerning the most appropriate form of metals upon which to base water quality standards. On October 1, 1993, EPA issued guidance on this issue which indicated that measuring the dissolved form of metal is the recommended approach. This new policy however, is prospective and does not affect the criteria in the National Toxics Rule. Dissolved metals criteria are not generally numerically equal to total recoverable criteria and the October 1, 1993 guidance contains recommendations for correction factors for fresh water criteria. The determination of site-specific criteria is applicable to criteria expressed as either total recoverable metal or as dissolved metal.

DISCUSSION

Existing guidance and practice are that EPA will approve site- specific criteria developed using appropriate procedures. That policy continues for the options set forth in the interim guidance transmitted today, regardless of whether the resulting criterion is equal to or more or less stringent than the EPA national 304(a) guidance. This interim guidance supersedes all guidance concerning water-effect ratios previously issued by the Agency.

Each of the three options for deriving a final water-effect ratio presented in this interim guidance meets the scientific and technical acceptability test for deriving site-specific criteria.

Option 3 is the simplest, least restrictive and generally the least expensive approach for situations where simulated downstream water appropriately represents a "site." It is a fully acceptable approach for deriving the water-effect ratio although it will generally provide a lower water-effect ratio than the other 2 options. The other 2 options may be more costly and time consuming if more than 3 sample periods and water-effect ratio measurements are made, but are more accurate, and may yield a larger, but more scientifically defensible site specific criterion.

Site-specific criteria, properly determined, will fully protect existing uses. The waterbody or segment thereof to which the site-specific criteria apply must be clearly defined. A site can be defined by the State and can be any size, small or large, including a watershed or basin. However, the site-specific criteria must protect the site as a whole. It is likely to be more cost-effective to derive any site-specific criteria for as large an area as possible or appropriate. It is emphasized that site-specific criteria are ambient water quality criteria applicable to a site. They are not intended to be direct modifications to National Pollutant Discharge Elimination System (NPDES) permit limits. In most cases the "site" will be synonymous with a State's "segment" in its water quality standards. By defining sites on a larger scale, multiple dischargers can collaborate on water-effect ratio testing and attain appropriate site-specific criteria at a reduced cost.

More attention has been given to water-effect ratios recently because of the numerous discussions and meetings on the entire question of metals policy and because WERs were specifically applied in the National Toxics Rule. In comments on the proposed National Toxics Rule, the public questioned whether the EPA promulgation should be based solely on the total recoverable form of a metal. For the reasons set forth in the final preamble, EPA chose to promulgate the criteria based on the total recoverable form with a provision for the application of a water-effect ratio. In addition, this approach was chosen because of the unique difficulties of attempting to authorize site-specific criteria modifications for nationally promulgated criteria.

EPA now recommends the use of dissolved metals for States revising their water quality standards. Dissolved criteria may also be modified by a site-specific adjustment.

While the regulatory application of the water-effect ratio applied only to the 10 jurisdictions included in the final National Toxics Rule for aquatic life metals criteria, we understood that other States would be interested in applying WERs to their adopted water quality standards. The guidance upon which to base the judgment of the acceptability of the water-effect ratio applied by the State is contained in the attached Interim Guidance on The Determination and Use of Water-Effect Ratios for Metals. It should be noted that this guidance also provides additional information on the recalculation procedure for site-specific criteria modifications.

Status of the Water-effect Ratio (WER) in non-National Toxics Rule States

A central question concerning WERs is whether their use by a State results in a site-specific criterion subject to EPA review and approval under Section 303(c) of the Clean Water Act?

Derivation of a water-effect ratio by a State is a site-specific criterion adjustment subject to EPA review and approval/disapproval under Section 303(c). There are two options by which this review can be accomplished.

> Option 1: A State may derive and submit each individual water-effect ratio determination to EPA for review and approval. This would be accomplished through the normal review and revision process used by a State.
>
> Option 2: A State can amend its water quality standards to provide a formal procedure which includes derivation of water-effect ratios, appropriate definition of sites, and enforceable monitoring provisions to assure that designated uses are protected. Both this procedure and the resulting criteria would be subject to full public participation requirements. Public review of a site-specific criterion could be accomplished in conjunction with the public review required for permit issuance. EPA would review and approve/disapprove this protocol as a revised standard once. For public information, we recommend that once a year the State publish a list of site-specific criteria.

An exception to this policy applies to the waters of the jurisdictions included in the National Toxics Rule. The EPA review is not required for the jurisdictions included in the National Toxics Rule where EPA established the procedure for the State for application to the criteria promulgated. The National Toxics Rule was a formal rulemaking process with notice and comment by which EPA pre-authorized the use of a correctly applied water-effect ratio. That same process has not yet taken place in States not included in the National Toxics Rule.

However, the National Toxics Rule does not affect State authority to establish scientifically defensible procedures to determine Federally authorized WERs, to certify those WERs in NPDES permit proceedings, or to deny their application based on the State's risk management analysis.

As described in Section 131.36(b)(iii) of the water quality standards regulation (the official regulatory reference to the National Toxics Rule), the water-effect ratio is a site-specific calculation. As indicated on page 60866 of the preamble to the National Toxics Rule, the rule was constructed as a rebuttable presumption. The water-effect ratio is assigned a value of 1.0 until a different water-effect ratio is derived from suitable tests representative of conditions in the affected waterbody. It is the responsibility of the State to determine whether to rebut the assumed value of 1.0 in the National Toxics Rule and apply another value of the water-effect ratio in order to establish a site-specific criterion. The site-specific criterion is then used to develop appropriate NPDES permit limits. The rule thus provides a State with the flexibility to derive an appropriate site-specific criterion for specific waterbodies.

As a point of emphasis, although a water-effect ratio affects permit limits for individual dischargers, it is the State in all cases that determines if derivation of a site-specific criterion based on the water-effect ratio is allowed and it is the State that ensures that the calculations and data analysis are done completely and correctly.

CONCLUSION

This interim guidance explains and clarifies the use of site-specific criteria. It is issued as interim guidance because it will be included as part of the process underway for review and possible revision of the national aquatic life criteria development methodology guidelines. As part of that review, this interim guidance is subject to amendment based on comments, especially those from the users of the guidance. At the end of the guidelines revision process the guidance will be issued as "final."

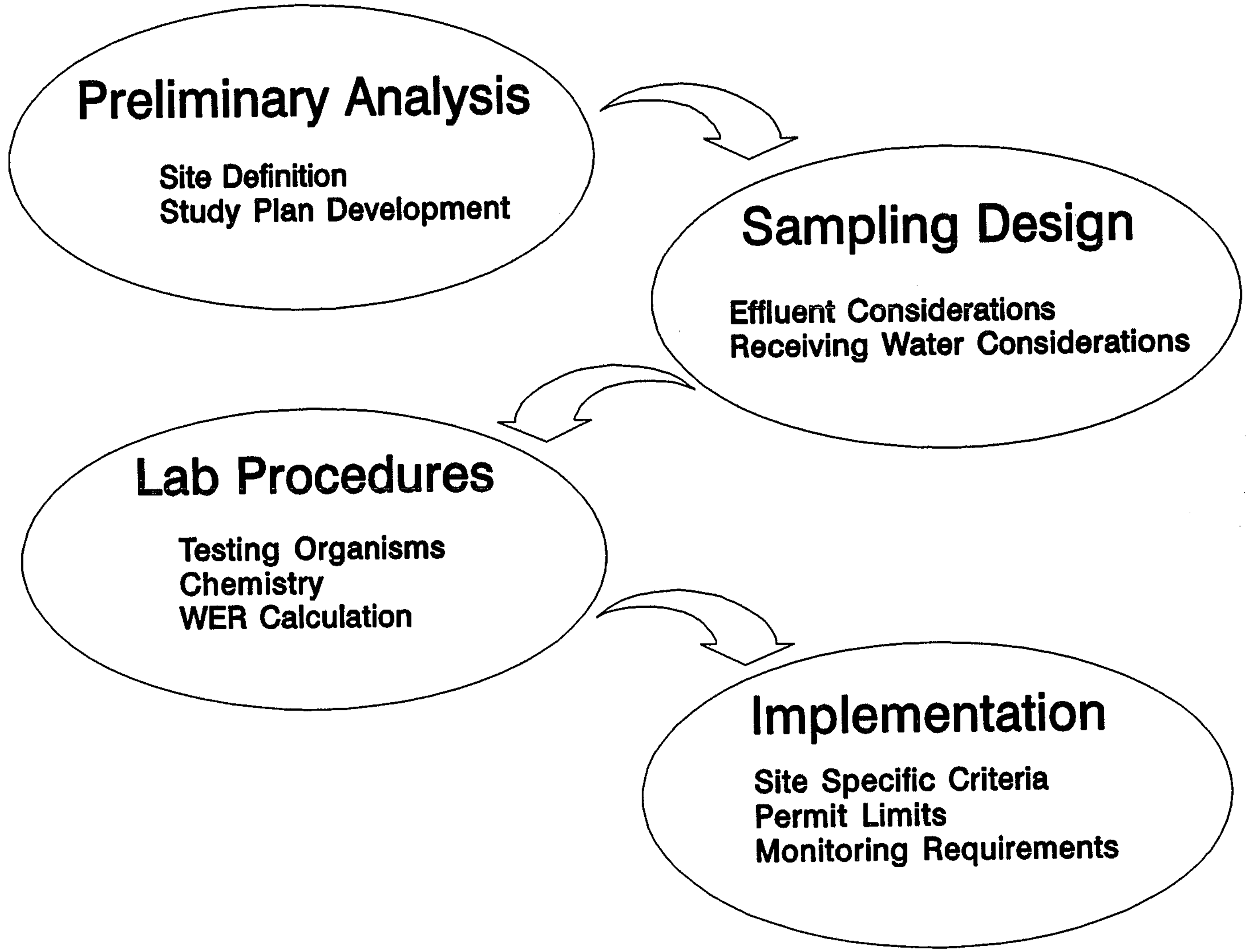
EPA is interested in and encourages the submittal of high quality datasets that can be used to provide insights into the use of these guidelines and procedures. Such data and technical comments should be submitted to Charles E. Stephan at EPA's Environmental Research Laboratory at Duluth, MN. A complete address, telephone number and fax number for Mr. Stephan are included in the guidance itself. Other questions or comments should be directed to the Standards and Applied Science Division (mail code 4305, telephone 202-260-1315).

There is attached to this memorandum a simplified flow diagram and an implementation procedure. These are intended to aid a user by placing the water-effect ratio procedure in the context of proceeding from at site-specific criterion to a permit limit. Following these attachments is the guidance itself.

Attachments

cc: Robert Perciasepe, OW
Martha G. Prothro, OW
William Diamond, SASD
Margaret Stasikowski, HECD
Mike Cook, OWEC
Cynthia Dougherty, OWEC
Lee Schroer, OGC
Susan Lepow, OGC
Courtney Riordan, ORD
ORD (Duluth and Narragansett Laboratories)
ESD Directors, Regions I - VIII, X
ESD Branch, Region IX
Water Quality Standards Coordinators, Regions I - X

WER Implementation



WATER-EFFECT RATIO IMPLEMENTATION

PRELIMINARY ANALYSIS & PLAN FORMULATION

- Site definition

  - How many discharges must be accounted for? Tributaries? See page 17.
  - What is the waterbody type? (i.e., stream, tidal river, bay, etc.). See page 44 and Appendix A.
  - How can these considerations best be combined to define the relevant geographic "site"? See Appendix A @ page 82.

- Plan Development for Regulatory Agency Review

  - Is WER method 1 or 2 appropriate? (e.g., Is design flow a meaningful concept or are other considerations paramount?). See page 6.
  - Define the effluent & receiving water sample locations
  - Describe the temporal sample collection protocols proposed. See page 48.
  - Can simulated site water procedure be done, or is downstream sampling required? See Appendix A.
  - Describe the testing protocols - test species, test type, test length, etc. See page 45, 50; Appendix I.
  - Describe the chemical testing proposed. See Appendix C.
  - Describe other details of study - flow measurement, QA/QC, number of sampling periods proposed, to whom the results are expected to apply, schedule, etc.

SAMPLING DESIGN FOR STREAMS

- Discuss the quantification of the design streamflow (e.g., 7Q10) - USGS gage directly, by extrapolation from USGS gage, or ?

- Effluents

  - measure flows to determine average for sampling day
  - collect 24 hour composite using "clean" equipment and appropriate procedures; avoid the use of the plant's daily composite sample as a shortcut.

- Streams

  - measure flow (use current meter or read from gage if available) to determine dilution with effluent; and to check if within acceptable range for use of the data (i.e., design flow to 10 times the design flow).
  - collect 24 hour composite of upstream water.

LABORATORY PROCEDURES (NOTE: These are described in detail in interim guidance).

- Select appropriate primary & secondary tests
- Determine appropriate cmcWER and/or cccWER
- Perform chemistry using clean procedures, with methods that have adequate sensitivity to measure low concentrations, and use appropriate QA/QC
- Calculate final water-effect ratio (FWER) for site. See page 36.

IMPLEMENTATION

- Assign FWERs and the site specific criteria for each metal to each discharger (if more than one).
- perform a waste load allocation and total maximum daily load (if appropriate) so that each discharger is provided a permit limit.
- establish monitoring condition for periodic evaluation of instream biology (recommended)
- establish a permit condition for periodic testing of WER to verify site-specific criterion (NTR recommendation)

Interim Guidance on

Determination and Use of

Water-Effect Ratios for Metals

February 1994

U.S. Environmental Protection Agency

Office of Water
Office of Science and Technology
Washington, D.C.

Office of Research and Development
Environmental Research Laboratories
Duluth, Minnesota
Narragansett, Rhode Island

NOTICES

This document has been reviewed by the Environmental Research Laboratories, Duluth, MN and Narragansett, RI (Office of Research and Development) and the Office of Science and Technology (Office of Water), U.S. Environmental Protection Agency, and approved for publication.

Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

This document provides interim guidance concerning the experimental determination of water-effect ratios (WERs) for metals; some aspects of the use of WERs are also addressed. It is issued in support of EPA regulations and policy initiatives involving the application of water quality criteria and standards for metals. This document is agency guidance only. It does not establish or affect legal rights or obligations. It does not establish a binding norm or prohibit alternatives not included in the document. It is not finally determinative of the issues addressed. Agency decisions in any particular case will be made by applying the law and regulations on the basis of specific facts when regulations are promulgated or permits are issued.

This document is expected to be revised periodically to reflect advances in this rapidly evolving area. Comments, especially those accompanied by supporting data, are welcomed and should be sent to: Charles E. Stephan, U.S. EPA, 6201 Congdon Boulevard, Duluth MN 55804 (TEL: 218-720-5510; FAX: 218-720-5539).

FEB 22 1994

OFFICE OF SCIENCE AND TECHNOLOGY POSITION STATEMENT

Section 131.11(b)(ii) of the water quality standards regulation (40 CFR Part 131) provides the regulatory mechanism for a State to develop site-specific criteria for use in water quality standards. Adopting site-specific criteria in water quality standards is a State option--not a requirement. The Environmental Protection Agency (EPA) in 1983 provided guidance on scientifically acceptable methods by which site-specific criteria could be developed.

The interim guidance provided in this document supersedes all guidance concerning water-effect ratios and the Indicator Species Procedure given in Chapter 4 of the *Water Quality Standards Handbook* issued by EPA in 1983 and in *Guidelines for Deriving Numerical Aquatic Site-Specific Water Quality Criteria by Modifying National Criteria, 1984*. Appendix B also supersedes the guidance in these earlier documents for the Recalculation Procedure for performing site-specific criteria modifications.

This interim guidance fulfills a commitment made in the final rule to establish numeric criteria for priority toxic pollutants (57 FR 60848, December 22, 1992, also known as the "National Toxics Rule"). This guidance also is applicable to pollutants other than metals with appropriate modifications, principally to chemical analyses.

Except for the jurisdictions subject to the aquatic life criteria in the national toxics rule, water-effect ratios are site-specific criteria subject to review and approval by the appropriate EPA Regional Administrator. Site-specific criteria are new or revised criteria subject to the normal EPA review requirements established in Clean Water Act § 303(c). For the States in the National Toxics Rule, EPA has established that site-specific water-effect ratios may be applied to the criteria promulgated in the rule to establish site-specific criteria. The water-effect ratio portion of these criteria would still be subject to State review before the development of total maximum daily loads, waste load allocations or translation into NPDES permit limits. EPA would only review these water-effect ratios during its oversight review of these State programs or review of State-issued permits.

Each of the three options for deriving a final water-effect ratio presented on page 36 of this interim guidance meets the scientific and technical acceptability test for deriving site-specific criteria specified in the water quality standards regulation (40 CFR 131.11(a)). Option 3 is the simplest, least restrictive and generally the least expensive approach for situations where simulated downstream water appropriately represents a "site." Option 3 requires experimental determination of three water-effect ratios with the primary test species that are determined during any season (as long as the downstream flow is between 2 and 10 times design flow conditions.) The final WER is generally (but not always) the lowest experimentally determined WER. Deriving a final water-effect ratio using option 3 with the use of simulated downstream water for a situation where this simulation appropriately represents a "site", is a fully acceptable approach for deriving a water-effect ratio for use in determining a site-specific criterion, although it will generally provide a lower water-effect ratio than the other 2 options.

As indicated in the introduction to this guidance, the determination of a water-effect ratio may require substantial resources. A discharger should consider cost-effective, preliminary measures described in this guidance (e.g., use of "clean" sampling and chemical analytical techniques or in non-NTR States, a recalculated criterion) to determine if an indicator species site-specific criterion is really needed. It may be that an appropriate site-specific criterion is actually being attained. In many instances, use of these other measures may eliminate the need for deriving final water-effect ratios. The methods described in this interim guidance should be sufficient to develop site-specific criteria that resolve concerns of dischargers when there appears to be no instream toxicity from a metal but, where (a) a discharge appears to exceed existing or proposed water quality-based permit limits, or (b) an instream concentration appears to exceed an existing or proposed water quality criterion.

This guidance describes 2 different methods for determining water-effect ratios. Method 1 has 3 options each of which may only require 3 sampling periods. However options 1 and 2 may be expanded and require a much greater effort. While this position statement has discussed the simplest, least expensive option for method 1 (the single discharge to a stream) to illustrate that site specific criteria are feasible even when only small dischargers are affected, water-effect ratios may be calculated using any of the other options described in the guidance if the State/discharger believe that there is reason to expect that a more accurate site-specific criterion will result from the increased cost and complexity inherent in conducting the additional tests and analyzing the results. Situations where this could be the case include, for example, where seasonal effects in receiving water quality or in discharge quality need to be assessed.

In addition, EPA will consider other scientifically defensible approaches in developing final water-effect ratios as authorized in 40 CFR 131.11. However, EPA strongly recommends that before a State/discharger implements any approach other than one described in this interim guidance, discussions be held with appropriate EPA regional offices and Office of Research and Development's scientists before actual testing begins. These discussions would be to ensure that time and resources are not wasted on scientifically and technically unacceptable approaches. It remains EPA's responsibility to make final decisions on the scientific and technical validity of alternative approaches to developing site-specific water quality criteria.

EPA is fully cognizant of the continuing debate between what constitutes guidance and what is a regulatory requirement. Developing site-specific criteria is a State regulatory option. Using the methodology correctly as described in this guidance assures the State that EPA will accept the result. Other approaches are possible and logically should be discussed with EPA prior to implementation.

The Office of Science and Technology believes that this interim guidance advances the science of determining site-specific criteria and provides policy guidance that States and EPA can use in this complex area. It reflects the scientific advances in the past 10 years and the experience gained from dealing with these issues in real world situations. This guidance will help improve implementation of water quality standards and be the basis for future progress.

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EXECUTIVE SUMMARY

A variety of physical and chemical characteristics of both the water and the metal can influence the toxicity of a metal to aquatic organisms in a surface water. When a site-specific aquatic life criterion is derived for a metal, an adjustment procedure based on the toxicological determination of a water-effect ratio (WER) may be used to account for a difference between the toxicity of the metal in laboratory dilution water and its toxicity in the water at the site. If there is a difference in toxicity and it is not taken into account, the aquatic life criterion for the body of water will be more or less protective than intended by EPA's Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses. After a WER is determined for a site, a site-specific aquatic life criterion can be calculated by multiplying an appropriate national, state, or recalculated criterion by the WER. Most WERs are expected to be equal to or greater than 1.0, but some might be less than 1.0. Because most aquatic life criteria consist of two numbers, i.e., a Criterion Maximum Concentration (CMC) and a Criterion Continuous Concentration (CCC), either a cmcWER or a cccWER or both might be needed for a site. The cmcWER and the cccWER cannot be assumed to be equal, but it is not always necessary to determine both.

In order to determine a WER, side-by-side toxicity tests are performed to measure the toxicity of the metal in two dilution waters. One of the waters has to be a water that would be acceptable for use in laboratory toxicity tests conducted for the derivation of national water quality criteria for aquatic life. In most situations, the second dilution water will be a simulated downstream water that is prepared by mixing upstream water and effluent in an appropriate ratio; in other situations, the second dilution water will be a sample of the actual site water to which the site-specific criterion is to apply. The WER is calculated by dividing the endpoint obtained in the site water by the endpoint obtained in the laboratory dilution water. A WER should be determined using a toxicity test whose endpoint is close to, but not lower than, the CMC and/or CCC that is to be adjusted.

A total recoverable WER can be determined if the metal in both of the side-by-side toxicity tests is analyzed using the total recoverable measurement, and a dissolved WER can be determined if the metal is analyzed in both tests using the dissolved measurement. Thus four WERs can be determined:

- Total recoverable cmcWER.
- Total recoverable cccWER.
- Dissolved cmcWER.
- Dissolved cccWER.

A total recoverable WER is used to calculate a total recoverable site-specific criterion from a total recoverable national, state, or recalculated aquatic life criterion, whereas a dissolved WER is used to calculate a dissolved site-specific criterion from a dissolved criterion. WERs are determined individually for each metal at each site; WERs cannot be extrapolated from one metal to another, one effluent to another, or one site water to another.

Because determining a WER requires substantial resources, the desirability of obtaining a WER should be carefully evaluated:

1. Determine whether use of "clean techniques" for collecting, handling, storing, preparing, and analyzing samples will eliminate the reason for considering determination of a WER, because existing data concerning concentrations of metals in effluents and surface waters might be erroneously high.
2. Evaluate the potential for reducing the discharge of the metal.
3. Investigate possible constraints on the permit limits, such as antibacksliding and antidegradation requirements and human health and wildlife criteria.
4. Consider use of the Recalculation Procedure.
5. Evaluate the cost-effectiveness of determining a WER.

If the determination of a WER is desirable, a detailed workplan for should be submitted to the appropriate regulatory authority (and possibly to the Water Management Division of the EPA Regional Office) for comment. After the workplan is completed, the initial phase should be implemented, the data should be evaluated, and the workplan should be revised if appropriate.

Two methods are used to determine WERs. Method 1, which is used to determine cccWERs that apply near plumes and to determine all cmcWERs, uses data concerning three or more distinctly separate sampling events. It is best if the sampling events occur during both low-flow and higher-flow periods. When sampling does not occur during both low and higher flows, the site-specific criterion is derived in a more conservative manner due to greater uncertainty. For each sampling event, a WER is determined using a selected toxicity test; for at least one of the sampling events, a confirmatory WER is determined using a different test.

Method 2, which is used to determine a cccWER for a large body of water outside the vicinities of plumes, requires substantial site-specific planning and more resources than Method 1. WERs are determined using samples of actual site water obtained at various times, locations, and depths to identify the range of WERs in the body of water. The WERs are used to determine how many site-specific CCCs should be derived for the body of water and what the one or more CCCs should be.

The guidance contained herein replaces previous agency guidance concerning (a) the determination of WERs for use in the derivation of site-specific aquatic life criteria for metals and (b) the Recalculation Procedure. This guidance is designed to apply to metals, but the principles apply to most pollutants.

ABBREVIATIONS

ACR: Acute-Chronic Ratio

CCC: Criterion Continuous Concentration

CMC: Criterion Maximum Concentration

CRM: Certified Reference Material

FAV: Final Acute Value

FCV: Final Chronic Value

FW: Freshwater

FWER: Final Water-Effect Ratio

GMAV: Genus Mean Acute Value

HCME: Highest Concentration of the Metal in the Effluent

MDR: Minimum Data Requirement

NTR: National Toxics Rule

QA/QC: Quality Assurance/Quality Control

SMAV: Species Mean Acute Value

SW: Saltwater

TDS: Total Dissolved Solids

TIE: Toxicity Identification Evaluation

TMDL: Total Maximum Daily Load

TOC: Total Organic Carbon

TRE: Toxicity Reduction Evaluation

TSD: Technical Support Document

TSS: Total Suspended Solids

WER: Water-Effect Ratio

WET: Whole Effluent Toxicity

WLA: Wasteload Allocation

GLOSSARY

Acute-chronic ratio - an appropriate measure of the acute toxicity of a material divided by an appropriate measure of the chronic toxicity of the same material under the same conditions.

Appropriate regulatory authority - Usually the State water pollution control agency, even for States under the National Toxics Rule; if, however, a State were to waive its section 401 authority, the Water Management Division of the EPA Regional Office would become the appropriate regulatory authority.

Clean techniques - a set of procedures designed to prevent contamination of samples so that concentrations of trace metals can be measured accurately and precisely.

Critical species - a species that is commercially or recreationally important at the site, a species that exists at the site and is listed as threatened or endangered under section 4 of the Endangered Species Act, or a species for which there is evidence that the loss of the species from the site is likely to cause an unacceptable impact on a commercially or recreationally important species, a threatened or endangered species, the abundances of a variety of other species, or the structure or function of the community.

Design flow - the flow used for steady-state wasteload allocation modeling.

Dissolved metal - defined here as "metal that passes through either a 0.45-μm or a 0.40-μm membrane filter".

Endpoint - the concentration of test material that is expected to cause a specified amount of adverse effect.

Final Water-Effect Ratio - the WER that is used in the calculation of a site-specific aquatic life criterion.

Flow-through test - a test in which test solutions flow into the test chambers either intermittently (every few minutes) or continuously and the excess flows out.

Labile metal - metal that is in water and will readily convert from one form to another when in a nonequilibrium condition.

Particulate metal - metal that is measured by the total recoverable method but not by the dissolved method.

Primary test - the toxicity test used in the determination of a Final Water-Effect Ratio (FWER); the specification of the test includes the test species, the life stage of the species, the duration of the test, and the adverse effect on which the endpoint is based.

Refractory metal - metal that is in water and will not readily convert from one form to another when in a nonequilibrium condition, i.e., metal that is in water and is not labile.

Renewal test - a test in which either the test solution in a test chamber is renewed at least once during the test or the test organisms are transferred into a new test solution of the same composition at least once during the test.

Secondary test - a toxicity test that is usually conducted along with the primary test only once to test the assumptions that, within experimental variation, (a) similar WERs will be obtained using tests that have similar sensitivities to the test material, and (b) tests that are less sensitive to the test material will usually give WERs that are closer to 1.

Simulated downstream water - a site water prepared by mixing effluent and upstream water in a known ratio.

Site-specific aquatic life criterion - a water quality criterion for aquatic life that has been derived to be specifically appropriate to the water quality characteristics and/or species composition at a particular location.

Site water - upstream water, actual downstream water, or simulated downstream water in which a toxicity test is conducted side-by-side with the same toxicity test in a laboratory dilution water to determine a WER.

Static test - a test in which the solution and organisms that are in a test chamber at the beginning of the test remain in the chamber until the end of the test.

Total recoverable metal - metal that is in aqueous solution after the sample is appropriately acidified and digested and insoluble material is separated.

Water-effect ratio - an appropriate measure of the toxicity of a material obtained in a site water divided by the same measure of the toxicity of the same material obtained simultaneously in a laboratory dilution water.

PREFACE

Several issues need consideration when guidance such as this is written:

1. Degrees of importance: Procedures and methods are series of instructions, but some of the instructions are more important than others. Some instructions are so important that, if they are not followed, the results will be questionable or unacceptable; other instructions are less important, but definitely desirable. Possibly the best way to express various degrees of importance is the approach described in several ASTM Standards, such as in section 3.6 of Standard E729 (ASTM 1993a), which is modified here to apply to WERs:

   The words "must", "should", "may", "can", and "might" have specific meanings in this document. "Must" is used to express an instruction that is to be followed, unless a site-specific consideration requires a deviation, and is used only in connection with instructions that directly relate to the validity of toxicity tests, WERs, FWERs, and the Recalculation Procedure. "Should" is used to state instructions that are recommended and are to be followed if reasonably possible. Deviation from one "should" will not invalidate a WER, but deviation from several probably will. Terms such as "is desirable", "is often desirable", and "might be desirable" are used in connection with less important instructions. "May" is used to mean "is (are) allowed to", "can" is used to mean "is (are) able to", and "might" is used to mean "could possibly". Thus the classic distinction between "may" and "can" is preserved, and "might" is not used as a synonym for either "may" or "can".

   This does not eliminate all problems concerning the degree of importance, however. For example, a small deviation from a "must" might not invalidate a WER, whereas a large deviation would. (Each "**must**" and "**must not**" is in bold print for convenience, not for emphasis, in this document.)

2. Educational and explanatory material: Many people have asked for much detail in this document to ensure that as many WERs as possible are determined in an acceptable manner. In addition, some people want justifications for each detail. Much of the detail that is desired by some people is based on "best professional judgment", which is rarely considered an acceptable justification by people who disagree with a specified detail. Even if details are taken from an EPA method or an ASTM standard, they were often included in those documents on the basis of best professional judgment. In contrast, some people want detailed methodology presented without explanatory material. It was decided to include as much detail as is feasible, and to provide rationale and explanation for major items.

3. Alternatives: When more than one alternative is both scientifically sound and appropriately protective, it seems reasonable to present the alternatives rather than presenting the one that is considered best. The reader can then select one based on cost-effectiveness, personal preference, details of the particular situation, and perceived advantages and disadvantages.

4. Separation of "science", "best professional judgment" and "regulatory decisions": These can never be completely separated in this kind of document; for example, if data are analyzed for a statistically significant difference, the selection of alpha is an important decision, but a rationale for its selection is rarely presented, probably because the selection is not a scientific decision. In this document, an attempt has been made to focus on good science, best professional judgment, and presentation of the rationale; when possible, these are separated from "regulatory decisions" concerning margin of safety, level of protection, beneficial use, regulatory convenience, and the goal of zero discharge. Some "regulatory decisions" relating to implementation, however, should be integrated with, not separated from, "science" because the two ought to be carefully considered together wherever science has implications for implementation.

5. Best professional judgment: Much of the guidance contained herein is qualitative rather than quantitative, and much judgment will usually be required to derive a site-specific water quality criterion for aquatic life. In addition, although this version of the guidance for determining and using WERs attempts to cover all major questions that have arisen during use of the previous version and during preparation of this version, it undoubtedly does not cover all situations, questions, and extenuating circumstances that might arise in the future. All necessary decisions should be based on both a thorough knowledge of aquatic toxicology and an understanding of this guidance; each decision should be consistent with the spirit of this guidance, which is to make best use of "good science" to derive the most appropriate site-specific criteria. This guidance should be modified whenever sound scientific evidence indicates that a site-specific criterion produced using this guidance will probably substantially underprotect or overprotect the aquatic life at the site of concern. Derivation of site-specific criteria for aquatic life is a complex process and requires knowledge in many areas of aquatic toxicology; any deviation from this guidance should be carefully considered to ensure that it is consistent with other parts of this guidance and with "good science".

6. Personal bias: Bias can never be eliminated, and some decisions are at the fine line between "bias" and "best

professional judgment". The possibility of bias can be eliminated only by adoption of an extreme position such as "no regulation" or "no discharge". One way to deal with bias is to have decisions made by a team of knowledgeable people.

7. Teamwork: The determination of a WER should be a cooperative team effort beginning with the completion of the initial workplan, interpretation of initial data, revision of the workplan, etc. The interaction of a variety of knowledgeable, reasonable people will help obtain the best results for the expenditure of the fewest resources. Members of the team should acknowledge their biases so that the team can make best use of the available information, taking into account its relevancy to the immediate situation and its quality.

INTRODUCTION

National aquatic life criteria for metals are intended to protect the aquatic life in almost all surface waters of the United States (U.S. EPA 1985). This level of protection is accomplished in two ways. First, the national dataset is required to contain aquatic species that have been found to be sensitive to a variety of pollutants. Second, the dilution water and the metal salt used in the toxicity tests are required to have physical and chemical characteristics that ensure that the metal is at least as toxic in the tests as it is in nearly all surface waters. For example, the dilution water is to be low in suspended solids and in organic carbon, and some forms of metal (e.g., insoluble metal and metal bound by organic complexing agents) cannot be used as the test material. (The term "metal" is used herein to include both "metals" and "metalloids".)

Alternatively, a national aquatic life criterion might not adequately protect the aquatic life at some sites. An untested species that is important at a site might be more sensitive than any of the tested species. Also, the metal might be more toxic in site water than in laboratory dilution water because, for example, the site water has a lower pH and/or hardness than most laboratory waters. Thus although a national aquatic life criterion is intended to be lower than necessary for most sites, a national criterion might not adequately protect the aquatic life at some sites.

Because a national aquatic life criterion might be more or less protective than intended for the aquatic life in most bodies of water, the U.S. EPA provided guidance (U.S. EPA 1983a,1984) concerning three procedures that may be used to derive a site-specific criterion:

1. The Recalculation Procedure is intended to take into account relevant differences between the sensitivities of the aquatic organisms in the national dataset and the sensitivities of organisms that occur at the site.
2. The Indicator Species Procedure provides for the use of a water-effect ratio (WER) that is intended to take into account relevant differences between the toxicity of the metal in laboratory dilution water and in site water.
3. The Resident Species Procedure is intended to take into account both kinds of differences simultaneously.

A site-specific criterion is intended to come closer than the national criterion to providing the intended level of protection to the aquatic life at the site, usually by taking into account the biological and/or chemical conditions (i.e., the species composition and/or water quality characteristics) at the site. The fact that the U.S. EPA has made these procedures available should not be interpreted as implying that the agency advocates that states derive site-specific criteria before setting state standards. Also, derivation of a site-specific criterion does not change the intended level of protection of the aquatic life at the site. Because a WER is expected to appropriately take into account (a) the site-specific toxicity of the metal, and (b) synergism, antagonism, and additivity with other constituents of the site water, using a WER is more likely to provide the intended level of protection than not using a WER.

Although guidance concerning site-specific criteria has been available since 1983 (U.S. EPA 1983a,1984), interest has increased in recent years as states have devoted more attention to chemical-specific water quality criteria for aquatic life. In addition, interest in water-effect ratios (WERs) increased when the "Interim Guidance" concerning metals (U.S. EPA 1992) made a fundamental change in the way that WERs are experimentally determined (see Appendix A), because the change is expected to substantially increase the magnitude of many WERs. Interest was further focused on WERs when they were integrated into some of the aquatic life criteria for metals that were promulgated by the National Toxics Rule (57 FR 60848, December 22, 1992). The newest guidance issued by the U.S. EPA (Prothro 1993) concerning aquatic life criteria for metals affected the determination and use of WERs only insofar as it affected the use of total recoverable and dissolved criteria.

The early guidance concerning WERs (U.S. EPA 1983a,1984) contained few details and needs revision, especially to take into account newer guidance concerning metals (U.S. EPA 1992; Prothro 1993). The guidance presented herein supersedes all guidance concerning WERs and the Indicator Species Procedure given in Chapter 4 of the Water Quality Standards Handbook (U.S. EPA 1983a) and in U.S. EPA (1984). All guidance presented in U.S. EPA (1992) is superseded by that presented by Prothro (1993) and by this document. Metals are specifically addressed herein because of the National Toxics Rule (NTR) and because of current interest in aquatic life criteria for metals; although most of this guidance also applies to other pollutants, some obviously applies only to metals.

Even though this document was prepared mainly because of the NTR, the guidance contained herein concerning WERs is likely to have impact beyond its use with the NTR. Therefore, it is appropriate to also present new guidance concerning the Recalculation Procedure (see Appendix B) because the previous guidance (U.S. EPA 1983a,1984) concerning this procedure also contained few details and needs revision. The NTR does not allow use of the Recalculation Procedure in jurisdictions subject to the NTR.

The previous guidance concerning site-specific procedures did not allow the Recalculation Procedure and the WER procedure to be used together in the derivation of a site-specific aquatic life criterion; the only way to take into account both species composition and water quality characteristics in the determination of a site-specific criterion was to use the Resident Species Procedure. A specific change contained herein is that, except in jurisdictions that are subject to the NTR, the Recalculation Procedure and the WER Procedure may now be used together. Additional reasons for addressing both the Recalculation Procedure and the WER Procedure in this document are that both procedures are based directly on the guidelines for deriving national aquatic life criteria (U.S. EPA 1985) and, when the two are used together, use of the Recalculation Procedure has specific implications concerning the determination of the WER.

This guidance is intended to produce WERs that may be used to derive site-specific aquatic life criteria for metals from most national and state aquatic life criteria that were derived from laboratory toxicity data. Except in jurisdictions that are subject to the NTR, the WERs may also be used with site-specific aquatic life criteria that are derived for metals using the Recalculation Procedure described in Appendix B. WERs obtained using the methods described herein should not be used to adjust aquatic life criteria that were derived for metals in other ways. For example, because they are designed to be applied to criteria derived on the basis of laboratory toxicity tests, WERs determined using the methods described herein cannot be used to adjust the residue-based mercury Criterion Continuous Concentration (CCC) or the field-based selenium freshwater criterion. For the purposes of the NTR, WERs may be used with the aquatic life criteria for arsenic, cadmium, chromium(III), chromium(VI), copper, lead, nickel, silver, and zinc and with the Criterion Maximum Concentration (CMC) for mercury. WERs may also be used with saltwater criteria for selenium.

The concept of a WER is rather simple:

> Two side-by-side toxicity tests are conducted - one test using laboratory dilution water and the other using site water. The endpoint obtained using site water is divided by the endpoint obtained using laboratory dilution water. The quotient is the WER, which is multiplied times the national, state, or recalculated aquatic life criterion to calculate the site-specific criterion.

Although the concept is simple, the determination and use of WERs involves many considerations.

The primary purposes of this document are to:

1. Identify steps that should be taken before the determination of a WER is begun.
2. Describe the methods recommended by the U.S. EPA for the determination of WERs.
3. Address some issues concerning the use of WERs.
4. Present new guidance concerning the Recalculation Procedure.

Before Determining a WER

Because a national criterion is intended to protect aquatic life in almost all bodies of water and because a WER is intended to account for a difference between the toxicity of a metal in a laboratory dilution water and its toxicity in a site water, dischargers who want higher permit limits than those derived on the basis of an existing aquatic life criterion will probably consider determining a WER. Use of a WER should be considered only as a last resort for at least three reasons:

a. Even though some WERs will be substantially greater than 1.0, some will be about 1.0 and some will be less than 1.0.
b. The determination of a WER requires substantial resources.
c. There are other things that a discharger can do that might be more cost-effective than determining a WER.

The two situations in which the determination of a WER might appear attractive to dischargers are when (a) a discharge appears to exceed existing or proposed water quality-based permit limits, and (b) an instream concentration appears to exceed an existing or proposed aquatic life criterion. Such situations result from measurement of the concentration of a metal in an effluent or a surface water. It would therefore seem reasonable to ensure that such measurements were not subject to contamination. Usually it is much easier to verify chemical measurements by using "clean techniques" for collecting, handling, storing, preparing, and analyzing samples, than to determine a WER. Clean techniques and some related QA/QC considerations are discussed in Appendix C.

In addition to investigating the use of "clean techniques", other steps that a discharger should take prior to beginning the experimental determination of a WER include:

1. Evaluate the potential for reducing the discharge of the metal.
2. Investigate such possible constraints on permit limits as antibacksliding and antidegradation requirements and human health and wildlife criteria.
3. Obtain assistance from an aquatic toxicologist who understands the basics of WERs (see Appendix D), the U.S. EPA's national aquatic life guidelines (U.S. EPA 1985), the guidance presented by Prothro (1993), the national criteria document for the metal(s) of concern (see Appendix E), the procedures described by the U.S. EPA (1993a,b,c) for acute and chronic toxicity tests on effluents and surface waters, and the procedures described by ASTM (1993a,b,c,d,e) for acute and chronic toxicity tests in laboratory dilution water.
4. Develop an initial definition of the site to which the site-specific criterion is to apply.
5. Consider use of the Recalculation Procedure (see Appendix B).
6. Evaluate the cost-effectiveness of the determination of a WER. Comparative toxicity tests provide the most useful data, but chemical analysis of the downstream water might be helpful

because the following are often true for some metals:

a. The lower the percent of the total recoverable metal in the downstream water that is dissolved, the higher the WER.

b. The higher the concentration of total organic carbon (TOC) and/or total suspended solids (TSS), the higher the WER.

It is also true that the higher the concentration of nontoxic dissolved metal, the higher the WER. Although some chemical analyses might provide useful information concerning the toxicities of some metals in water, at the present only toxicity tests can accurately reflect the toxicities of different forms of a metal (see Appendix D).

7. Submit a workplan for the experimental determination of the WER to the appropriate regulatory authority (and possibly to the Water Management Division of the EPA Regional Office) for comment. The workplan should include detailed descriptions of the site; existing criterion and standard; design flows; site water; effluent; sampling plan; procedures that will be used for collecting, handling, and analyzing samples of site water and effluent; primary and secondary toxicity tests; quality assurance/quality control (QA/QC) procedures; Standard Operating Procedures (SOPs); and data interpretation.

After the workplan is completed, the initial phase should be implemented; then the data obtained should be evaluated, and the workplan should be revised if appropriate. Developing and modifying the workplan and analyzing and interpreting the data should be a cooperative effort by a team of knowledgeable people.

Two Kinds of WERs

Most aquatic life criteria contain both a CMC and a CCC, and it is usually possible to determine both a cmcWER and a cccWER. The two WERs cannot be assumed to be equal because the magnitude of a WER will probably depend on the sensitivity of the toxicity test used and on the percent effluent in the site water (see Appendix D), both of which can depend on which WER is to be determined. In some cases, it is expected that a larger WER can be applied to the CCC than to the CMC, and so it would be environmentally conservative to apply cmcWERs to CCCs. In such cases it is possible to determine a cmcWER and apply it to both the CMC and the CCC in order to derive a site-specific CMC, a site-specific CCC, and new permit limits. If these new permit limits are controlled by the new site-specific CCC, a cccWER could be determined using a more sensitive test, possibly raising the site-specific CCC and the permit limits again. A cccWER may, of course, be determined whenever desired. Unless the experimental variation is increased, use of a cccWER will usually improve the accuracy of the resulting site-specific CCC.

In some cases, a larger WER cannot be applied to the CCC than to the CMC and so it might not be environmentally conservative to apply a cmcWER to a CCC (see section A.4 of Method 1).

Steady-state and Dynamic Models

Some of the guidance contained herein specifically applies to situations in which the permit limits were calculated using steady-state modeling; in particular, some samples are to be obtained when the actual stream flow is close to the design flow. If permit limits were calculated using dynamic modeling, the guidance will have to be modified, but it is unclear at present what modifications are most appropriate. For example, it might be useful to determine whether the magnitude of the WER is related to the flow of the upstream water and/or the effluent.

Two Methods

Two methods are used to determine WERs. Method 1 will probably be used to determine all cmcWERs and most cccWERs because it can be applied to situations that are in the vicinities of plumes. Because WERs are likely to depend on the concentration of effluent in the water and because the percent effluent in a water sample obtained in the immediate vicinity of a plume is unknown, simulated downstream water is used so that the percent effluent in the sample is known. For example, if a sample that was supposed to represent a complete-mix situation was accidently taken in the plume upstream of complete mix, the sample would probably have a higher percent effluent and a higher WER than a sample taken downstream of complete mix; use of the higher WER to derive a site-specific criterion for the complete-mix situation would result in underprotection. If the sample were accidently taken upstream of complete mix but outside the plume, overprotection would probably result.

Method 1 will probably be used to determine all cmcWERs and most cccWERs in flowing fresh waters, such as rivers and streams. Method 1 is intended to apply not only to ordinary rivers and streams but also to streams that some people might consider extraordinary, such as streams whose design flows are zero and streams that some state and/or federal agencies refer to as "effluent-dependent", "habitat-creating", or "effluent-dominated". Method 1 is also used to determine cmcWERs in such large sites as oceans and large lakes, reservoirs, and estuaries (see Appendix F).

Method 2 is used to determine WERs that apply outside the area of plumes in large bodies of water. Such WERs will be cccWERs and will be determined using samples of actual site water obtained at various times, locations, and depths in order to identify the range of WERs that apply to the body of water. These experimentally determined WERs are then used to decide how many site-specific criteria should be derived for the body of water and what the criterion (or criteria) should be. Method 2 requires substantially more resources than Method 1.

The complexity of each method increases when the number of metals and/or the number of discharges is two or more:

a. The simplest situation is when a WER is to be determined for only one metal and only one discharge has permit limits for that metal. (This is the single-metal single-discharge situation.)
b. A more complex situation is when a WER is to be determined for only one metal, but more than one discharge has permit limits for that metal. (This is the single-metal multiple-discharge situation.)
c. An even more complex situation is when WERs are to be determined for more than one metal, but only one discharge has permit limits for any of the metals. (This is the multiple-metal single-discharge situation.)
d. The most complex situation is when WERs are to be determined for more than one metal and more than one discharge has permit limits for some or all of the metals. (This is the multiple-metal multiple-discharge situation.)

WERs need to be determined for each metal at each site because extrapolation of a WER from one metal to another, one effluent to another, or one surface water to another is too uncertain.

Both methods work well in multiple-metal situations, but special tests or additional tests will be necessary to show that the resulting combination of site-specific criteria will not be too toxic. Method 2 is better suited to multiple-discharge situations than is Method 1. Appendix F provides additional guidance concerning multiple-metal and multiple-discharge situations, but it does not discuss allocation of waste loads, which is performed when a wasteload allocation (WLA) or a total maximum daily load (TMDL) is developed (U.S. EPA 1991a).

Two Analytical Measurements

A total recoverable WER can be determined if the metal in both of the side-by-side toxicity tests is analyzed using the total recoverable measurement; similarly, a dissolved WER can be determined if the metal in both tests is analyzed using the dissolved measurement. A total recoverable WER is used to calculate a total recoverable site-specific criterion from an aquatic life criterion that is expressed using the total recoverable measurement, whereas a dissolved WER is used to calculate a dissolved site-specific criterion from a criterion that is expressed in terms of the dissolved measurement. Figure 1 illustrates the relationships between total recoverable and dissolved criteria, WERs, and the Recalculation Procedure.

Both Method 1 and Method 2 can be used to determine a total recoverable WER and/or a dissolved WER. The only difference in the experimental procedure is whether the WER is based on measurements of total recoverable metal or dissolved metal in the test solutions. Both total recoverable and dissolved measurements are to be performed for all tests to help judge the quality of the tests, to provide a check on the analytical chemistry, and to help understand the results; performing both measurements also increases the alternatives available for use of the results. For example, a dissolved WER that is not useful with a total recoverable criterion might be useful in the future if a dissolved criterion becomes available. Also, as explained in Appendix D, except for experimental variation, use of a total recoverable WER with a total recoverable criterion should produce the same total recoverable permit limits as use of a dissolved WER with a dissolved criterion; the internal consistency of the approaches and the data can be evaluated if both total recoverable and dissolved criteria and WERs are determined. It is expected that in many situations total recoverable WERs will be larger and more variable than dissolved WERs.

The Quality of the Toxicity Tests

Traditionally, for practical reasons, the requirements concerning such aspects as acclimation of test organisms to test temperature and dilution water have not been as stringent for toxicity tests on surface waters and effluents as for tests using laboratory dilution water. Because a WER is a ratio calculated from the results of side-by-side tests, it might seem that acclimation is not important for a WER as long as the organisms and conditions are identical in the two tests. Because WERs are used to adjust aquatic life criteria that are derived from results of laboratory tests, the tests conducted in laboratory dilution water for the determination of WERs should be conducted in the same way as the laboratory toxicity tests used in the derivation of aquatic life criteria. In the WER process, the tests in laboratory dilution water provide the vital link between national criteria and site-specific criteria, and so it is important to compare at least some results obtained in the laboratory dilution water with results obtained in at least one other laboratory.

Three important principles for making decisions concerning the methodology for the side-by-side tests are:

1. The tests using laboratory dilution water should be conducted so that the results would be acceptable for use in the derivation of national criteria.
2. As much as is feasible, the tests using site water should be conducted using the same procedures as the tests using the laboratory dilution water.
3. All tests should follow any special requirements that are necessary because the results are to be used to calculate a WER. Some such special requirements are imposed because the criterion for a rather complex situation is being changed based on few data, so more assurance is required that the data are high quality.

The most important special requirement is that the concentrations of the metal are to be measured using both the total recoverable and dissolved methods in all toxicity tests used for the determination of a WER. This requirement is necessary because half of the tests conducted for the determination of WERs use a site water in which the concentration of metal probably is not negligible. Because it is likely that the concentration of metal in the laboratory dilution water is negligible, assuming that the concentration in both waters is negligible and basing WERs on the amount of metal added would produce an unnecessarily low value for the WER. In addition, WERs are based on too few data to assume that nominal concentrations are accurate. Nominal concentrations obviously cannot be used if a dissolved WER is to be determined. Measured dissolved concentrations at the beginning and end of the test are used to judge the acceptability of the test, and it is certainly reasonable to measure the total recoverable concentration when the dissolved concentration is measured. Further, measuring the concentrations might lead to an interpretation of the results that allows a substantially better use of the WERs.

Conditions for Determining a WER

The appropriate regulatory authority might recommend that one or more conditions be met when a WER is determined in order to reduce the possibility of having to determine a new WER later:

1. Requirements that are in the existing permit concerning WET testing, Toxicity Identification Evaluation (TIE), and/or Toxicity Reduction Evaluation (TRE) (U.S. EPA 1991a).
2. Implementation of pollution prevention efforts, such as pretreatment, waste minimization, and source reduction.
3. A demonstration that applicable technology-based requirements are being met.

If one or more of these is not satisfied when the WER is determined and is implemented later, it is likely that a new WER will have to be determined because of the possibility of a change in the composition of the effluent.

Even if all recommended conditions are satisfied, determination of a WER might not be possible if the effluent, upstream water, and/or downstream water are toxic to the test organisms. In some such cases, it might be possible to determine a WER, but remediation of the toxicity is likely to be required anyway. It is unlikely that a WER determined before remediation would be considered acceptable for use after remediation. If it is desired to determine a WER before remediation and the toxicity is in the upstream water, it might be possible to use a laboratory dilution water or a water from a clean tributary in place of the upstream water; if a substitute water is used, its water quality characteristics should be similar to those of the upstream water (i.e., the pH should be within 0.2 pH units and the hardness, alkalinity, and concentrations of TSS and TOC should be within 10 % or 5 mg/L, whichever is greater, of those in the upstream water). If the upstream water is chronically toxic, but not acutely toxic, it might be possible to determine a cmcWER even if a cccWER cannot be determined; a cmcWER might not be useful, however, if the permit limits are controlled by the CCC; in such a case, it would probably not be acceptable to assume that the cmcWER is an environmentally conservative estimate of the cccWER. If the WER is determined using downstream water and the toxicity is due to the effluent, tests at lower concentrations of the effluent might give an indication of the amount of remediation needed.

Conditions for Using a WER

Besides requiring that the WER be valid, the appropriate regulatory authority might consider imposing other conditions for the approval of a site-specific criterion based on the WER:

1. Periodic reevaluation of the WER.
   a. WERs determined in upstream water take into account constituents contributed by point and nonpoint sources and natural runoff; thus a WER should be reevaluated whenever newly implemented controls or other changes substantially affect such factors as hardness, alkalinity, pH, suspended solids, organic carbon, or other toxic materials.
   b. Most WERs determined using downstream water are influenced more by the effluent than the upstream water. Downstream WERs should be reevaluated whenever newly implemented controls or other changes might substantially impact the effluent, i.e., might impact the forms and concentrations of the metal, hardness, alkalinity, pH, suspended solids, organic carbon, or other toxic materials. A special concern is the possibility of a shift from discharge of nontoxic metal to discharge of toxic metal such that the concentration of the metal does not increase; analytical chemistry might not detect the change but toxicity tests would.

   Even if no changes are known to have occurred, WERs should be reevaluated periodically. (The NTR recommends that NPDES permits include periodic determinations of WERs in the monitoring requirements.) With advance planning, it should usually be possible to perform such reevaluations under conditions that are at least reasonably similar to those that control the permit limits (e.g., either design-flow or high-flow conditions) because there should be a reasonably long period of time during which the reevaluation can be performed. Periodic determination of WERs should be designed to answer questions, not just generate data.
2. Increased chemical monitoring of the upstream water, effluent, and/or downstream water, as appropriate, for water quality characteristics that probably affect the toxicity of the metal

(e.g., hardness, alkalinity, pH, TOC, and TSS) to determine whether conditions change. The conditions at the times the samples were obtained should be kept on record for reference. The WER should be reevaluated whenever hardness, alkalinity, pH, TOC, and/or TSS decrease below the values that existed when the WERs were determined.

3. Periodic reevaluation of the environmental fate of the metal in the effluent (see Appendix A).
4. WET testing.
5. Instream bioassessments.

Decisions concerning the possible imposition of such conditions should take into account:

a. The ratio of the new and old criteria. The greater the increase in the criterion, the more concern there should be about (1) the fate of any nontoxic metal that contributes to the WER and (2) changes in water quality that might occur within the site. The imposition of one or more conditions should be considered if the WER is used to raise the criterion by, for example, a factor of two, and especially if it is raised by a factor of five or more. The significance of the magnitude of the ratio can be judged by comparison with the acute-chronic ratio, the factor of two that is the ratio of the FAV to the CMC, and the range of sensitivities of species in the criteria document for the metal (see Appendix E).
b. The size of the site.
c. The size of the discharge.
d. The rate of downstream dilution.
e. Whether the CMC or the CCC controls the permit limits.

When WERs are determined using upstream water, conditions on the use of a WER are more likely when the water contains an effluent that increases the WER by adding TOC and/or TSS, because the WER will be larger and any decrease in the discharge of such TOC and/or TSS might decrease the WER and result in underprotection. A WER determined using downstream water is likely to be larger and quite dependent on the composition of the effluent; there should be concern about whether a change in the effluent might result in underprotection at some time in the future.

Implementation Considerations

In some situations a discharger might not want to or might not be allowed to raise a criterion as much as could be justified by a WER:

1. The maximum possible increase is not needed and raising the criterion more than needed might greatly raise the cost if a greater increase would require more tests and/or increase the conditions imposed on approval of the site-specific criterion.
2. Such other constraints as antibacksliding or antidegradation requirements or human health or wildlife criteria might limit the amount of increase regardless of the magnitude of the WER.

3. The permit limits might be limited by an aquatic life criterion that applies outside the site. It is EPA policy that permit limits cannot be so high that they inadequately protect a portion of the same or a different body of water that is outside the site; nothing contained herein changes this policy in any way.

If no increase in the existing discharge is allowed, the only use of a WER will be to determine whether an existing discharge needs to be reduced. Thus a major use of WERs might be where technology-based controls allow concentrations in surface waters to exceed national, state, or recalculated aquatic life criteria. In this case, it might only be necessary to determine that the WER is greater than a particular value; it might not be necessary to quantify the WER. When possible, it might be desirable to show that the maximum WER is greater than the WER that will be used in order to demonstrate that a margin of safety exists, but again it might not be necessary to quantify the maximum WER.

In jurisdictions not subject to the NTR, WERs should be used to derive site-specific criteria, not just to calculate permit limits, because data obtained from ambient monitoring should be interpreted by comparison with ambient criteria. (This is not a problem in jurisdictions subject to the NTR because the NTR defines the ambient criterion as "WER x the EPA criterion".) If a WER is used to adjust permit limits without adjusting the criterion, the permit limits would allow the criterion to be exceeded. Thus the WER should be used to calculate a site-specific criterion, which should then be used to calculate permit limits. In some states, site-specific criteria can only be adopted as revised criteria in a separate, independent water quality standards review process. In other states, site-specific criteria can be developed in conjunction with the NPDES permitting process, as long as the adoption of a site-specific criterion satisfies the pertinent water quality standards procedural requirements (i.e., a public notice and a public hearing). In either case, site-specific criteria are to be adopted prior to NPDES permit issuance. Moreover, the EPA Regional Administrator has authority to approve or disapprove all new and revised site-specific criteria and to review NPDES permits to verify compliance with the applicable water quality criteria.

Other aspects of the use of WERs in connection with permit limits, WLAs, and TMDLs are outside the scope of this document. The Technical Support Document (U.S. EPA 1991a) and Prothro (1993) provide more information concerning implementation procedures. Nothing contained herein should be interpreted as changing the three-part approach that EPA uses to protect aquatic life: (1) numeric chemical-specific water quality criteria for individual pollutants, (2) whole effluent toxicity (WET) testing, and (3) instream bioassessments.

Even though there are similarities between WET testing and the determination of WERs, there are important differences. For example, WERs can be used to derive site-specific criteria for individual pollutants, but WET testing cannot. The difference between WET testing and the determination of WERs is less when the toxicity tests used in the determination of the WER are ones that are used in WET testing. If a WER is used to make a large change in a criterion, additional WET testing and/or instream bioassessments are likely to be recommended.

The Sample-Specific WER Approach

A major problem with the determination and use of aquatic life criteria for metals is that no analytical measurement or combination of measurements has yet been shown to explain the toxicity of a metal to aquatic plants, invertebrates, amphibians, and fishes over the relevant range of conditions in surface waters (see Appendix D). It is not just that insufficient data exist to justify a relationship; rather, existing data possibly contradict some ideas that could possibly be very useful if true. For example, the concentration of free metal ion could possibly be a useful basis for expressing water quality criteria for metals if it could be feasible and could be used in a way that does not result in widespread underprotection of aquatic life. Some available data, however, might contradict the idea that the toxicity of copper to aquatic organisms is proportional to the concentration or the activity of the cupric ion. Evaluating the usefulness of any approach based on metal speciation is difficult until it is known how many of the species of the metal are toxic, what the relative toxicities are, whether they are additive (if more than one is toxic), and the quantitative effects of the factors that have major impacts on the bioavailability and/or toxicity of the toxic species. Just as it is not easy to find a useful quantitative relationship between the analytical chemistry of metals and the toxicity of metals to aquatic life, it is also not easy to find a qualitative relationship that can be used to provide adequate protection for the aquatic life in almost all bodies of water without providing as much overprotection for some bodies of water as results from use of the total recoverable and dissolved measurements.

The U.S. EPA cannot ignore the existence of pollution problems and delay setting aquatic life criteria until all scientific issues have been adequately resolved. In light of uncertainty, the agency needs to derive criteria that are environmentally conservative in most bodies of water. Because of uncertainty concerning the relationship between the analytical chemistry and the toxicity of metals, aquatic life criteria for metals are expressed in terms of analytical measurements that result in the criteria providing more protection than necessary for the aquatic life in most bodies of water. The agency has provided for the use of WERs to address the general conservatism, but expects that some WERs will be less than 1.0 because national, state, and recalculated criteria are not necessarily environmentally conservative for all bodies of water.

It has become obvious, however, that the determination and use of WERs is not a simple solution to the existing general conservatism. It is likely that a permanent solution will have to be based on an adequate quantitative explanation of how metals and aquatic organisms interact. In the meantime, the use of total recoverable and dissolved measurements to express criteria and the use of site-specific criteria are intended to provide adequate protection for almost all bodies of water without excessive overprotection for too many bodies of water. Work needs to continue on the permanent solution and, just in case, on improved alternative approaches.

Use of WERs to derive site-specific criteria is intended to allow a reduction or elimination of the general overprotection associated with application of a national criterion to individual bodies of water, but a major problem is that a WER will rarely be constant over time, location, and depth in a body of water due to plumes, mixing, and resuspension. It is possible that dissolved concentrations and WERs will be less variable than total recoverable ones. It might also be possible to reduce the impact of the heterogeneity if WERs are additive across time, location, and depth (see Appendix G). Regardless of what approaches, tools, hypotheses, and assumptions are utilized, variation will exist and WERs will have to be used in a conservative manner. Because of variation between bodies of water, national criteria are derived to be environmentally conservative for most bodies of water, whereas the WER procedure, which is intended to reduce the general conservatism of national criteria, has to be conservative because of variation among WERs within a body of water.

The conservatism introduced by variation among WERs is due not to the concept of WERs, but to the way they are used. The reason that national criteria are conservative in the first place is the uncertainty concerning the linkage of analytical chemistry and toxicity; the toxicity of solutions can be measured, but toxicity cannot be modelled adequately using available chemical measurements. Similarly, the current way that WERs are used depends on a linkage between analytical chemistry and toxicity because WERs are used to derive site-specific criteria that are expressed in terms of chemical measurements.

Without changing the amount or kind of toxicity testing that is performed when WERs are determined using Method 2, a different way of using the WERs could avoid some of the problems introduced by the dependence on analytical chemistry. The "sample-specific WER approach" could consist of sampling a body of water at a number of locations, determining the WER for each sample, and measuring the concentration of the metal in each sample. Then for each individual sample, a quotient would be calculated by dividing the concentration of metal in the sample by the product of the national criterion times the WER obtained for that sample. Except for experimental variation, when the quotient for a sample is less than 1, the concentration of metal in that sample is acceptable; when the quotient for a sample is greater than 1, the concentration of metal in that sample is too high. As a check, both the total recoverable measurement and the dissolved measurement should be used because they should provide the same answer if everything is done correctly and accurately. This approach can also be used whenever Method 1 is used; although Method 1 is used with simulated downstream water, the sample-specific WER approach can be used with either simulated downstream water or actual downstream water.

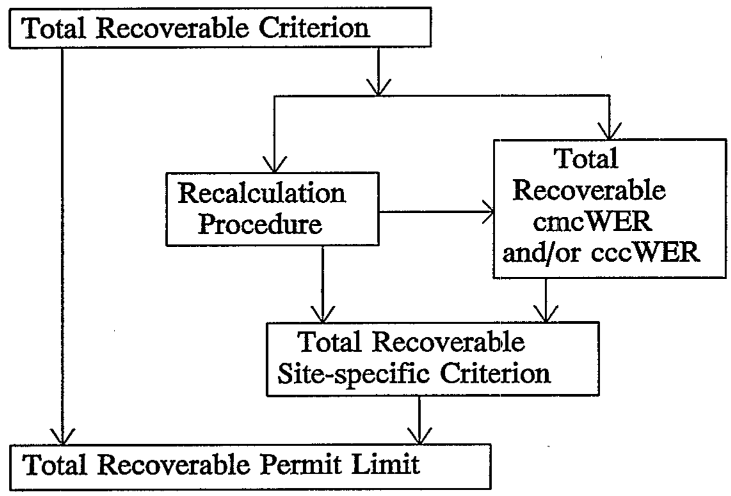
This sample-specific WER approach has several interesting features:

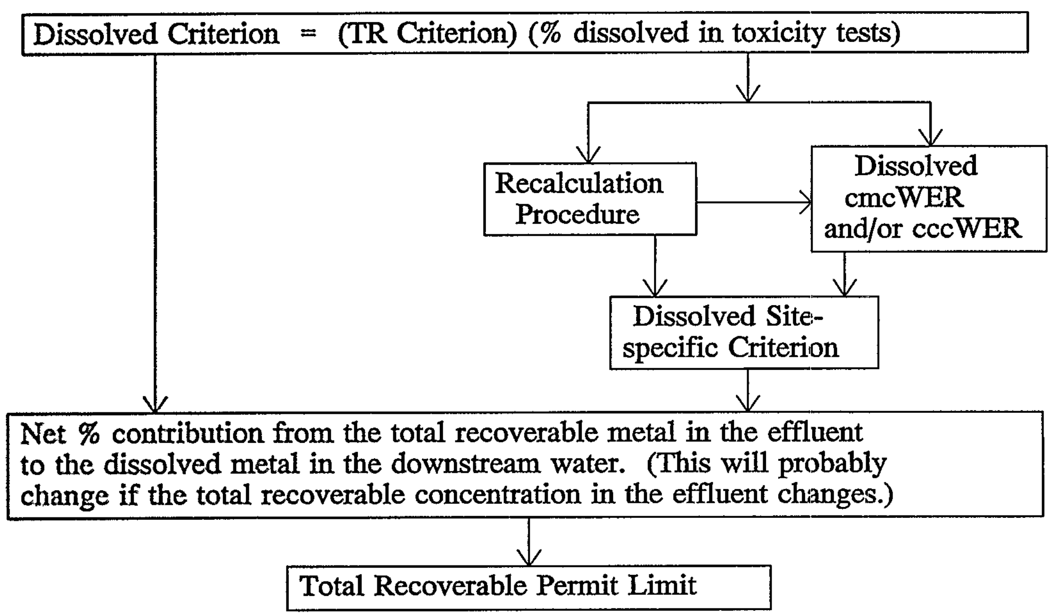
1. It is not a different way of determining WERs; it is merely a different way of using the WERs that are determined.
2. Variation among WERs within a body of water is not a problem.
3. It eliminates problems concerning the unknown relationship between toxicity and analytical chemistry.
4. It works equally well in areas that are in or near plumes and in areas that are away from plumes.
5. It works equally well in single-discharge and multiple-discharge situations.
6. It automatically accounts for synergism, antagonism, and additivity between toxicants.

This way of using WERs is equivalent to expressing the national criterion for a pollutant in terms of toxicity tests whose endpoints equal the CMC and the CCC; if the site water causes less adverse effect than is defined to be the endpoint, the concentration of that pollutant in the site water does not exceed the national criterion. This sample-specific WER approach does not directly fit into the current framework wherein criteria are derived and then permit limits are calculated from the criteria.

If the sample-specific WER approach were to produce a number of quotients that are greater than 1, it would seem that the concentration of metal in the discharge(s) should be reduced enough that the quotient is not greater than 1. Although this might sound straightforward, the discharger(s) would find that a substantial reduction in the discharge of a metal would not achieve the intended result if the reduction was due to removal of nontoxic metal. A chemical monitoring approach that cannot differentiate between toxic and nontoxic metal would not detect that only nontoxic metal had been removed, but the sample-specific WER approach would.

Figure 1: Four Ways to Derive a Permit Limit





For both the total recoverable and dissolved measurements, derivation of an optional site-specific criterion is described on the right. If both the Recalculation Procedure and the WER procedure are used, the Recalculation Procedure must be performed first. (The Recalculation Procedure cannot be used in jurisdictions that are subject to the National Toxics Rule.)

METHOD 1: DETERMINING WERs FOR AREAS IN OR NEAR PLUMES

Method 1 is based on the determination of WERs using simulated downstream water and so it can be used to determine a WER that applies in the vicinity of a plume. Use of simulated downstream water ensures that the concentration of effluent in the site water is known, which is important because the magnitude of the WER will often depend on the concentration of effluent in the downstream water. Knowing the concentration of effluent makes it possible to quantitatively relate the WER to the effluent. Method 1 can be used to determine either cmcWERs or cccWERs or both in single-metal, flowing freshwater situations, including streams whose design flow is zero and "effluent-dependent" streams (see Appendix F). As is also explained in Appendix F, Method 1 is used when cmcWERs are determined for "large sites", although Method 2 is used when cccWERs are determined for "large sites". In addition, Appendix F addresses special considerations regarding multiple-metal and/or multiple-discharge situations.

Neither Method 1 nor Method 2 covers all important methodological details for conducting the side-by-side toxicity tests that are necessary in order to determine a WER. Many references are made to information published by the U.S. EPA (1993a,b,c) concerning toxicity tests on effluents and surface waters and by ASTM (1993a,b,c,d,e,f) concerning tests in laboratory dilution water. Method 1 addresses aspects of toxicity tests that (a) need special attention when determining WERs and/or (b) are usually different for tests conducted on effluents and tests conducted in laboratory dilution water. Appendix H provides additional information concerning toxicity tests with saltwater species.

A. Experimental Design

Because of the variety of considerations that have important implications for the determination of a WER, decisions concerning experimental design should be given careful attention and need to answer the following questions:

1. Should WERs be determined using upstream water, actual downstream water, and/or simulated downstream water?
2. Should WERs be determined when the stream flow is equal to, higher than, and/or lower than the design flow?
3. Which toxicity tests should be used?
4. Should a cmcWER or a cccWER or both be determined?
5. How should a FWER be derived?
6. For metals whose criteria are hardness-dependent, at what hardness should WERs be determined?

The answers to these questions should be based on the reason that WERs are determined, but the decisions should also take into account some practical considerations.

1. Should WERs be determined using upstream water, actual downstream water, and/or simulated downstream water?

   a. Upstream water provides the least complicated way of determining and using WERs because plumes, mixing zones, and effluent variability do not have to be taken into account. Use of upstream water provides the least useful WERs because it does not take into account the presence of the effluent, which is the source of the metal. It is easy to assume that upstream water will give smaller WERs than downstream water, but in some cases downstream water might give smaller WERs (see Appendix G). Regardless of whether upstream water gives smaller or larger WERs, a WER should be determined using the water to which the site-specific criterion is to apply (see Appendix A).

   b. Actual downstream water might seem to be the most pertinent water to use when WERs are determined, but whether this is true depends on what use is to be made of the WERs. WERs determined using actual downstream water can be quantitatively interpreted using the sample-specific WER approach described at the end of the Introduction. If, however, it is desired to understand the quantitative implications of a WER for an effluent of concern, use of actual downstream water is problematic because the concentration of effluent in the water can only be known approximately.

      Sampling actual downstream water in areas that are in or near plumes is especially difficult. The WER obtained is likely to depend on where the sample is taken because the WER will probably depend on the percent effluent in the sample (see Appendix D). The sample could be taken at the end of the pipe, at the edge of the acute mixing zone, at the edge of the chronic mixing zone, or in a completely mixed situation. If the sample is taken at the edge of a mixing zone, the composition of the sample will probably differ from one point to another along the edge of the mixing zone.

      If samples of actual downstream water are to be taken close to a discharge, the mixing patterns and plumes should be well known. Dye dispersion studies (Kilpatrick 1992) are commonly used to determine isopleths of effluent concentration and complete mix; dilution models (U.S. EPA 1993d) might also be helpful when selecting sampling locations. The most useful samples of actual downstream water are probably those taken just downstream of the point at which complete mix occurs or at the most distant point that is within the site to which the site-specific criterion is to apply. When samples are collected from a complete-mix situation, it might be appropriate to composite samples taken over a cross section of the stream. Regardless of where it is decided conceptually that a sample should be taken, it might be difficult to identify where the point exists in the stream and how it changes with flow and over time. In addition, if it is not known exactly what the sample actually represents, there is no way to know how reproducible the sample is. These problems make it difficult to relate WERs determined in actual downstream water to an effluent of concern because the concentration of effluent in the sample is not known; this is not a problem, however, if the sample-specific WER approach is used to interpret the results.

c. Simulated downstream water would seem to be the most unnatural of the three kinds of water, but it offers several important advantages because effluent and upstream water are mixed at a known ratio. This is important because the magnitude of the WER will often depend on the concentration of effluent in the downstream water. Mixtures can be prepared to simulate the ratio of effluent and upstream water that exists at the edge of the acute mixing zone, at the edge of the chronic mixing zone, at complete mix, or at any other point of interest. If desired, a sample of effluent can be mixed with a sample on upstream water in different ratios to simulate different points in a stream. Also, the ratio used can be one that simulates conditions at design flow or at any other flow.

The sample-specific WER approach can be used with both actual and simulated downstream water. Additional quantitative uses can be made of WERs determined using simulated downstream water because the percent effluent in the water is known, which allows quantitative extrapolations to the effluent. In addition, simulated downstream water can be used to determine the variation in the WER that is due to variation in the effluent. It also allows comparison of two or more effluents and determination of the interactions of two or more effluents. Additivity of WERs can be studied using simulated downstream water (see Appendix G); studies of toxicity within plumes and studies of whether increased flow of upstream water can increase toxicity are both studies of additivity of WERs. Use of simulated downstream water also makes it possible to conduct controlled studies of changes in WERs due to aging and changes in pH.

In Method 1, therefore, WERs are determined using simulated downstream water that is prepared by mixing samples of effluent and upstream water in an appropriate ratio. Most importantly, Method 1 can be used to determine a WER that applies in the vicinity of a plume and can be quantitatively extrapolated to the effluent.

2. Should WERs be determined when the stream flow is equal to, higher than, and/or lower than the design flow?

WERs are used in the derivation of site-specific criteria when it is desired that permit limits be based on a criterion that takes into account the characteristics of the water and/or the metal at the site. In most cases, permit limits are calculated using steady-state models and are based on a design flow. It is therefore important that WERs be adequately protective under design-flow conditions, which might be expected to require that some sets of samples of effluent and upstream water be obtained when the actual stream flow is close to the design flow. Collecting samples when the stream flow is close to the design flow will limit a WER determination to the low-flow season (e.g., from mid-July to mid-October in some places) and to years in which the flow is sufficiently low.

It is also important, however, that WERs that are applied at design flow provide adequate protection at higher flows. Generalizations concerning the impact of higher flows on WERs are difficult because such flows might (a) reduce hardness, alkalinity, and pH, (b) increase or decrease the concentrations of TOC and TSS, (c) resuspend toxic and/or nontoxic metal from the sediment, and (d) wash additional pollutants into the water. Acidic snowmelt, for example, might lower the WER both by diluting the WER and by reducing the hardness, alkalinity, and pH; if substantial labile metal is present, the WER might be lowered more than the concentration of the metal, possibly resulting in increased toxicity at flows higher than design flow. Samples taken at higher flows might give smaller WERs because the concentration of the effluent is more dilute; however, total recoverable WERs might be larger if the sample is taken just after an event that greatly increases the concentration of TSS and/or TOC because this might increase both (1) the concentration of nontoxic particulate metal in the water and (2) the capacity of the water to sorb and detoxify metal.

WERs are not of concern when the stream flow is lower than the design flow because these are acknowledged times of reduced protection. Reduced protection might not occur, however, if the WER is sufficiently high when the flow is lower than design flow.

3. Which toxicity tests should be used?

a. As explained in Appendix D, the magnitude of an experimentally determined WER is likely to depend on the sensitivity of the toxicity test used. This relationship between the magnitude of the WER and the sensitivity of the toxicity test is due to the aqueous chemistry of metals and is not related to the test organisms or the type of test. The available data indicate that WERs determined with different tests do not differ greatly if the tests have about the same sensitivities, but the data also support the generalization that less sensitive toxicity tests usually give smaller WERs than more sensitive tests (see Appendix D).

b. When the CCC is lower than the CMC, it is likely that a larger WER will result from tests that are sensitive at the CCC than from tests that are sensitive at the CMC.

c. The considerations concerning the sensitivities of two tests should also apply to two endpoints for the same test. For any lethality test, use of the LC25 is likely to result in a larger WER than use of the LC50, although the difference might not be measurable in most cases and the LC25 is likely to be more variable than the LC50. Selecting the percent effect to be used to define the endpoint might take into account (a) whether the endpoint is above or below the CMC and/or the CCC and (b) the data obtained when tests are conducted. Once the percent effect is selected for a particular test (e.g., a 48-hr LC50 with 1-day-old fathead minnows), the same percent effect **must** be used whenever that test is used to determine a WER for that effluent. Similarly, if two different tests with the same species (e.g., a lethality test and a sublethal test) have substantially different sensitivities, both a cmcWER and a cccWER could be obtained with the same species.

d. The <u>primary</u> toxicity test used in the determination of a WER should have an endpoint in laboratory dilution water that is close to, but <u>not lower</u> than, the CMC and/or CCC to which the WER is to be applied.

e. Because the endpoint of the primary test in laboratory dilution water cannot be lower than the CMC and/or CCC, the magnitude of the WER is likely to become closer to 1 as the endpoint of the primary test becomes closer to the CMC and/or CCC (see Appendix D).

f. The WER obtained with the primary test should be confirmed with a <u>secondary</u> test that uses a species that is taxonomically different from the species used in the primary test.

   1) The endpoint of the secondary test may be <u>higher or lower</u> than the CMC, the CCC, or the endpoint of the primary test.

2) Because of the limited number of toxicity tests that have sensitivities near the CMC or CCC for a metal, it seems unreasonable to require that the two species be further apart taxonomically than being in different orders.

Two different endpoints with the same species **must not** be used as the primary and secondary tests, even if one endpoint is lethal and the other is sublethal.

g. If more sensitive toxicity tests generally give larger WERs than less sensitive tests, the maximum value of a WER will usually be obtained using a toxicity test whose endpoint in laboratory dilution water equals the CMC or CMC. If such a test is not used, the maximum possible WER probably will not be obtained.

h. No rationale exists to support the idea that different species or tests with the same sensitivity will produce different WERs. Because the mode of action might differ from species to species and/or from effect to effect, it is easy to speculate that in some cases the magnitude of a WER will depend to some extent on the species, life stage, and/or kind of test, but no data are available to support conclusions concerning the existence and/or magnitude of any such differences.

i. If the tests are otherwise acceptable, both cmcWERs and cccWERs may be determined using acute and/or chronic tests and using lethal and/or sublethal endpoints. The important consideration is the sensitivity of the test, not the duration, species, life stage, or adverse effect used.

j. There is no reason to use species that occur at the site; they may be used in the determination of a WER if desired, but:
   1) It might be difficult to determine which of the species that occur at the site are sensitive to the metal and are adaptable to laboratory conditions.
   2) Species that occur at the site might be harder to obtain in sufficient numbers for conducting toxicity tests over the testing period.
   3) Additional QA tests will probably be needed (see section C.3.b) because data are not likely to be available from other laboratories for comparison with the results in laboratory dilution water.

k. Because a WER is a ratio of results obtained with the same test in two different dilution waters, toxicity tests that are used in WET testing, for example, may be used, even if the national aquatic life guidelines (U.S. EPA 1985) do not allow use of the test in the derivation of an aquatic life criterion. Of course, a test whose endpoint in laboratory dilution water is below the CMC and/or CCC that is to be adjusted cannot be used as a primary test.

l. Because there is no rationale that suggest that it makes any difference whether the test is conducted with a species that is warmwater or coldwater, a fish or an invertebrate, or resident or nonresident at the site, other than the fact that less sensitive tests are likely to give smaller WERs, such considerations as the availability of test organisms might be important in the selection of the test. Information in Appendix I, a criteria document for the metal of concern (see Appendix E), or any other pertinent source might be useful when selecting primary and secondary tests.
m. A test in which the test organisms are not fed might give a different WER than a test in which the organisms are fed just because of the presence of the food (see Appendix D). This might depend on the metal, the type and amount of food, and whether a total recoverable or dissolved WER is determined.

Different tests with similar sensitivities are expected to give similar WERs, except for experimental variation. The purpose of the secondary test is to provide information concerning this assumption and the validity of the WER.

4. Should a cmcWER or a cccWER or both be determined?

This question does not have to be answered if the criterion for the site contains either a CMC or a CCC but not both. For example, a body of water that is protected for put-and-take fishing might have only a CMC, whereas a stream whose design flow is zero might have only a CCC.

When the criterion contains both a CMC and a CCC, the simplistic way to answer the question is to determine whether the CMC or the CCC controls the existing permit limits; which one is controlling depends on (a) the ratio of the CMC to the CCC, (b) whether the number of mixing zones is zero, one, or two, and (c) which steady-state or dynamic model was used in the calculation of the permit limits. A better way to answer the question would be to also determine how much the controlling value would have to be changed for the other value to become controlling; this might indicate that it would not be cost-effective to derive, for example, a site-specific CMC (ssCMC) without also deriving a site-specific CCC (ssCCC). There are also other possibilities: (1) It might be appropriate to use a phased approach, i.e., determine either the cmcWER or the cccWER and then decide whether to determine the other. (2) It might be appropriate and environmentally conservative to determine a WER that can be applied to both the CMC and the CCC. (3) It is always allowable to determine and use both a cmcWER and a cccWER, although both can be determined only if toxicity tests with appropriate sensitivities are available.

Because the phased approach can always be used, it is only important to decide whether to use a different approach when its use might be cost-effective. Deciding whether to use a different approach and selecting which one to use is complex because a number of considerations need to be taken into account:

a. Is the CMC equal to or higher than the CCC?
   If the CMC equals the CCC, two WERs cannot be determined if they would be determined using the same site water, but two WERs could be determined if the cmcWER and the cccWER would be determined using different site waters, e.g., waters that contain different concentrations of the effluent.

b. If the CMC is higher than the CCC, is there a toxicity test whose endpoint in laboratory dilution water is between the CMC and the CCC?
   If the CMC is higher than the CCC and there is a toxicity test whose endpoint in laboratory dilution water is between the CMC and the CCC, both a cmcWER and a cccWER can be determined. If the CMC is higher than the CCC but no toxicity test has an endpoint in laboratory dilution water between the CMC and the CCC, two WERs cannot be determined if they would be determined using the same site water; two WERs could be determined if they were determined using different site waters, e.g., waters that contain different concentrations of the effluent.

c. Was a steady-state or a dynamic model used in the calculation of the permit limits?
   It is complex, but reasonably clear, how to make a decision when a steady-state model was used, but it is not clear how a decision should be made when a dynamic model was used.

d. If a steady-state model was used, were one or two design flows used, i.e., was the hydrologically based steady-state method used or was the biologically based steady-state method used?
   When the hydrologically based method is used, one design flow is used for both the CMC and the CCC, whereas when the biologically based method is used, there is a CMC design flow and a CCC design flow. When WERs are determined using downstream water, use of the biologically based method will probably cause the percent effluent in the site water used in the determination of the cmcWER to be different from the percent effluent in the site water used in the determination of the cccWER; thus the two WERs should be determined using two different site waters. This does not impact WERs determined using upstream water.

e. Is there an acute mixing zone? Is there a chronic mixing zone?
   1. When WERs are determined using upstream water, the presence or absence of mixing zones has no impact; the cmcWER and the cccWER will both be determined using site water that contains zero percent effluent, i.e., the two WERs will be determined using the same site water.
   2. Even when downstream water is used, whether there is an acute mixing zone affects the point of application of the CMC or ssCMC, but it does not affect the determination of any WER.
   3. The existence of a chronic mixing zone has important implications for the determination of WERs when downstream water is used (see Appendix A). When WERs are determined using downstream water, the cmcWER should be determined using water at the edge of the chronic mixing zone, whereas the cccWER should be determined using water from a complete-mix situation. (If the biologically based method is used, the two different design flows should also be taken into account when determining the percent effluent that should be in the simulated downstream water.) Thus the percent effluent in the site water used in the determination of the cmcWER will be different from the percent effluent in the site water used in the determination of the cccWER; this is important because the magnitude of a WER will often depend substantially on the percent effluent in the water (see Appendix D).

f. In what situations would it be environmentally conservative to determine one WER and use it to adjust both the cmcWER and the cccWER?

   Because (1) the CMC is never lower than the CCC and (2) a more sensitive test will generally give a WER closer to 1, it will be environmentally conservative to use a cmcWER to adjust a CCC when there are no contradicting considerations. In this case, a cmcWER can be determined and used to adjust both the CMC and the CCC. Because water quality can affect the WER, this approach is necessarily valid only if the cmcWER and the cccWER are determined in the same site water. Other situations in which it would be environmentally conservative to use one WER to adjust both the CMC and the CCC are described below.

These considerations have one set of implications when both the cmcWER and cccWER are to be determined using the same site water, and another set of implications when the two WERs are to be determined using different site waters, e.g., when the site waters contain different concentrations of effluent.

When WERs are determined using upstream water, the same site water is used in the determination of both the cmcWER and the cccWER. Whenever the two WERs are determined in the same site water, any difference in the magnitude of the cmcWER and the cccWER will probably be due to the sensitivities of the toxicity tests used. Therefore:

a. If more sensitive toxicity tests generally give larger WERs than less sensitive tests, the maximum cccWER (a cccWER determined with a test whose endpoint equals the CCC) will usually be larger than the maximum cmcWER because the CCC is never higher than the CMC.
b. Because the CCC is never higher than the CMC, the maximum cmcWER will usually be smaller than the maximum cccWER and it will be environmentally conservative to use the cmcWER to adjust the CCC.
c. A cccWER can be determined separately from a cmcWER only if there is a toxicity test with an endpoint in laboratory dilution water that is between the CMC and the CCC. If no such test exists or can be devised, only a cmcWER can be determined, but it can be used to adjust both the CMC and the CCC.
d. Unless the experimental variation is increased, use of a cccWER, instead of a cmcWER, to adjust the CCC will usually improve the accuracy of the resulting site-specific CCC. Thus a cccWER may be determined and used whenever desired, if a toxicity test has an endpoint in laboratory dilution water between the CMC and the CCC.
e. A cccWER cannot be used to adjust a CMC if the cccWER was determined using an endpoint that was lower than the CMC in laboratory dilution water because it will probably reduce the level of protection.
f. Even if there is a toxicity test that has an endpoint in laboratory dilution water that is between the CMC and the CCC, it is not necessary to decide initially whether to determine a cmcWER and/or a cccWER. When upstream water is used, it is always allowable to determine a cmcWER and use it to derive a site-specific CMC and a site-specific CCC and then decide whether to determine a cccWER.
g. If there is a toxicity test whose endpoint in laboratory dilution water is between the CCC and the CMC, and if this test is used as the secondary test in the determination of the cmcWER, this test will provide information that should be very useful for deciding whether to determine a cccWER in addition to a cmcWER. Further, if it is decided to determine a cccWER, the same two tests used in the determination of the cmcWER could then be used in the determination of the cccWER, with a reversal of their roles as primary and secondary tests. Alternatively, a cmcWER and a cccWER could be determined simultaneously if both tests are conducted on each sample of site water.

When WERs are determined using <u>downstream</u> water, the magnitude of each WER will probably depend on the concentration of effluent in the downstream water used (see Appendix D). The first important consideration is whether the design flow is greater than zero, and the second is whether there is a chronic mixing zone.

a. If the design flow is zero, cmcWERs and/or cccWERs that are determined for design-flow conditions will both be determined in 100 percent effluent. Thus this case is similar to using upstream water in that both WERs are determined in the same site water. When WERs are determined for high-flow conditions, it will make a difference whether a chronic mixing zone needs to be taken into account, which is the second consideration.
b. If there is no chronic mixing zone, both WERs will be determined for the complete-mix situation; this case is similar to using upstream water in that both WERs are determined using the same site water. If there is a chronic mixing zone, cmcWERs should be determined in the site water that exists at the edge of the chronic mixing zone, whereas cccWERs should be determined for the complete-mix situation (see Appendix A). Thus the percent effluent will be higher in the site water used in the determination of the cmcWER than in the site water used in the determination of the cccWER. Because a site water with a higher percent effluent will probably give a larger WER than a site water with a lower percent effluent, both a cmcWER and a cccWER can be determined even if there is no test whose endpoint in laboratory dilution water is between the CMC and the CCC. There are opposing considerations, however:
   1) The site water used in the determination of the cmcWER will probably have a higher percent effluent than the site water used in the determination of the cccWER, which will tend to cause the cmcWER to be larger than the cccWER.
   2) If there is a toxicity test whose endpoint in laboratory dilution water is between the CMC and the CCC, use of a more sensitive test in the determination of the cccWER will tend to cause the cccWER to be larger than the cmcWER.

One consequence of these opposing considerations is that it is not known whether use of the cmcWER to adjust the CCC would be environmentally conservative; if this simplification is not known to be conservative, it should not be used. Thus it is important whether there is a toxicity test whose endpoint in laboratory dilution water is between the CMC and the CCC:

a. If no toxicity test has an endpoint in laboratory dilution water between the CMC and the CCC, the two WERs have to be determined with the same test, in which case the cmcWER will probably be larger because the percent effluent in the site water will be higher. Because of the difference in percent effluent in the site waters that should be used in the determinations of the two WERs, use of the cmcWER to adjust the CCC would not be environmentally conservative, but use of the cccWER to adjust the CMC would be environmentally conservative. Although both WERs could be determined, it would also be acceptable to determine only the cccWER and use it to adjust both the CMC and the CCC.

b. If there is a toxicity test whose endpoint in laboratory dilution water is between the CMC and the CCC, the two WERs could be determined using different toxicity tests. An environmentally conservative alternative to determining two WERs would be to determine a hybrid WER by using (1) a toxicity test whose endpoint is above the CMC (i.e., a toxicity test that is appropriate for the determination of a cmcWER) and (2) site water for the complete-mix situation (i.e., site water appropriate for the determination of cccWER). It would be environmentally conservative to use this hybrid WER to adjust the CMC and it would be environmentally conservative to use this hybrid WER to adjust the CCC. Although both WERs could be determined, it would also be acceptable to determine only the hybrid WER and use it to adjust both the CMC and the CCC. (This hybrid WER described here in paragraph b is the same as the cccWER described in paragraph a above in which no toxicity test had an endpoint in laboratory dilution water between the CMC and the CCC.)

5. How should a FWER be derived?

<u>Background</u>

Because of experimental variation and variation in the composition of surface waters and effluents, a single determination of a WER does not provide sufficient information to justify adjustment of a criterion. After a sufficient number of WERs have been determined in an acceptable manner, a Final Water-Effect Ratio (FWER) is derived from the WERs, and the FWER is then used to calculate the site-specific criterion. If both a site-specific CMC and a site-specific CCC are to be derived, both a cmcFWER and a cccFWER have to be derived, unless an environmentally conservative estimate is used in place of the cmcFWER and/or the cccFWER.

When a WER is determined using upstream water, the two major sources of variation in the WER are (a) variability in the quality of the upstream water, much of which might be related to season and/or flow, and (b) experimental variation. When a WER is determined in downstream water, the four major sources of variation are (a) variability in the quality of the upstream water, much of which might be related to season and/or flow, (b) experimental variation, (c) variability in the composition of the effluent, and (d) variability in the percent effluent in the downstream water. Variability and the possibility of mistakes and rare events make it necessary to try to compromise between (1) providing a high probability of adequate protection and (2) placing too much reliance on the smallest experimentally determined WER, which might reflect experimental variation, a mistake, or a rare event rather than a meaningful difference in the WER.

Various ways can be employed to address variability:

a. Replication can be used to reduce the impact of some sources of variation and to verify the importance of others.
b. Because variability in the composition of the effluent might contribute substantially to the variability of the WER, it might be desirable to obtain and store two or more samples of the effluent at slightly different times, with the selection of the sampling times depending on such characteristics of the discharge as the average retention time, in case an unusual WER is obtained with the first sample used.
c. Because of the possibility of mistakes and rare events, samples of effluent and upstream water should be large enough that portions can be stored for later testing or analyses if an unusual WER is obtained.
d. It might be possible to reduce the impact of the variability in the percent effluent in the downstream water by establishing a relationship between the WER and the percent effluent.

Confounding of the sources can be a problem when more than one source contributes substantial variability.

When permit limits are calculated using a steady-state model, the limits are based on a design flow, e.g., the 7Q10. It is usually assumed that a concentration of metal in an effluent that does not cause unacceptable effects at the design flow will not cause unacceptable effects at higher flows because the metal is diluted by the increased flow of the upstream water. Decreased protection might occur, however, if an increase in flow increases toxicity more than it dilutes the concentration of metal. When permit limits are based on a national criterion, it is often assumed that the criterion is sufficiently conservative that an increase in toxicity will not be great enough to overwhelm the combination of dilution and the assumed conservatism, even though it is likely that the national criterion is not overprotective of all bodies of water. When WERs are used to reduce the assumed conservatism, there is more concern about the possibility of increased toxicity at flows higher than the design flow and it is important to (1) determine some WERs that correspond to higher flows or (2) provide some conservatism. If the concentration of effluent in the downstream water decreases as flow increases, WERs determined at higher flows are likely to be smaller than WERs determined at design flow but the concentration of metal will also be lower. If the concentration of TSS increases at high flows, however, both the WER and the concentration of metal might increase. If they are determined in an appropriate manner, WERs determined at flows higher than the design flow can be used in two ways:

a. As environmentally conservative estimates of WERs determined at design flow.
b. To assess whether WERs determined at design flow will provide adequate protection at higher flows.

In order to appropriately take into account seasonal and flow effects and their interactions, both ways of using high-flow WERs require that the downstream water used in the determination of the WER be similar to that which actually exists during the time of concern. In addition, high-flow WERs can be used in the second way only if the composition of the downstream water is known. To satisfy the requirements that (a) the downstream water used in the determination of a WER be similar to the actual water and (b) the composition of the downstream water be known, it is necessary to obtain samples of effluent and upstream water at the time of concern and to prepare a simulated downstream water by mixing the samples at the ratio of the flows of the effluent and the upstream water that existed when the samples were obtained.

For the first way of using high-flow WERs, they are used directly as environmentally conservative estimates of the design-flow WER. For the second way of using high-flow WERs, each is used to calculate the highest concentration of metal that could be in the effluent without causing the concentration of metal in the downstream water to exceed the site-specific criterion that would be derived for that water using the experimentally determined WER. This highest concentration of metal in the effluent (HCME) can be calculated as:

$$HCME = \frac{[(CCC)(WER)(eFLOW + uFLOW)] - [(uCONC)(uFLOW)]}{eFLOW} ,$$

where:

CCC = the national, state, or recalculated CCC (or CMC) that is to be adjusted.

eFLOW = the flow of the effluent that was the basis of the preparation of the simulated downstream water. This should be the flow of the effluent that existed when the samples were taken.

uFLOW = the flow of the upstream water that was the basis of the preparation of the simulated downstream water. This should be the flow of the upstream water that existed when the samples were taken.

uCONC = the concentration of metal in the sample of upstream water used in the preparation of the simulated downstream water.

In order to calculate a HCME from an experimentally determined WER, the only information needed besides the flows of the effluent and the upstream water is the concentration of metal in the upstream water, which should be measured anyway in conjunction with the determination of the WER.

When a steady-state model is used to derive permit limits, the limits on the effluent apply at all flows; thus, each HCME can be used to calculate the highest WER (hWER) that could be used to derive a site-specific criterion for the downstream water at design flow so that there would be adequate protection at the flow for which the HCME was determined. The hWER is calculated as:

$$hWER = \frac{(HCME)\,(eFLOWdf) + (uCONCdf)\,(uFLOWdf)}{(CCC)\,(eFLOWdf + uFLOWdf)} .$$

The suffix "df" indicates that the values used for these quantities in the calculation of the hWER are those that exist at design-flow conditions. The additional datum needed in order to calculate the hWER is the concentration of metal in upstream water at design-flow conditions; if this is assumed to be zero, the hWER will be environmentally conservative. If a WER is determined when uFLOW equals the design flow, hWER = WER.

The two ways of using WERs determined at flows higher than design flow can be illustrated using the following examples. These examples were formulated using the concept of additivity of WERs (see Appendix G). A WER determined in downstream water consists of two components, one due to the effluent (the eWER) and one due to the upstream water (the uWER). If the eWER and uWER are strictly additive, when WERs are determined at various upstream flows, the downstream WERs can be calculated from the composition of the downstream water (the % effluent and the % upstream water) and the two WERs (the eWER and the uWER) using the equation:

$$WER = \frac{(\%\ effluent)(eWER) + (\%\ upstream\ water)(uWER)}{100}\ .$$

In the examples below, it is assumed that:
a. A site-specific CCC is being derived.
b. The national CCC is 2 ug/L.
c. The eWER is 40.
d. The eWER and uWER are constant and strictly additive.
e. The flow of the effluent (eFLOW) is always 10 cfs.
f. The design flow of the upstream water (uFLOWdf) is 40 cfs.

Therefore:

$$HCME = \frac{[(2\ ug/L)(WER)(10\ cfs + uFLOW)] - [(uCONC)(uFLOW)]}{10\ ug/L}\ .$$

$$hWER = \frac{(HCME)(10\ cfs) + (uCONCdf)(40\ cfs)}{(2\ ug/L)(10\ cfs + 40\ cfs)}\ .$$

In the first example, the uWER is assumed to be 5 and so the upstream site-specific CCC (ussCCC) = (CCC)(uWER) = (2 ug/L)(5) = 10 ug/L. uCONC is assumed to be 0.4 ug/L, which means that the assimilative capacity of the upstream water is 9.6 ug/L.

eFLOW	uFLOW	At Complete Mix			HCME	hWER
(cfs)	(cfs)	% Eff.	% Ups.	WER	(ug/L)	
10	40	20.0	80.0	12.000	118.4	12.00
10	63	13.7	86.3	9.795	140.5	14.21
10	90	10.0	90.0	8.500	166.4	16.80
10	190	5.0	95.0	6.750	262.4	26.40
10	490	2.0	98.0	5.700	550.4	55.20
10	990	1.0	99.0	5.350	1030.4	103.20
10	1990	0.5	99.5	5.175	1990.4	199.20

As the flow of the upstream water increases, the WER decreases to a limiting value equal to uWER. Because the assimilative capacity is greater than zero, the HCMEs and hWERs increase due to the increased dilution of the effluent. The increase in hWER at higher flows will not allow any use of the assimilative capacity of the upstream water because the allowed concentration of metal in the effluent is controlled by the lowest hWER, which is the design-flow hWER in this example. Any WER determined at a higher flow can be used as an environmentally conservative estimate of the design-flow WER, and the hWERs show that the WER of 12 provides adequate protection at all flows. When uFLOW equals the design flow of 40 cfs, WER = hWER.

In the second example, uWER is assumed to be 1, which means that ussCCC = 2 ug/L. uCONC is assumed to be 2 ug/L, so that uCONC = ussCCC. The assimilative capacity of the upstream water is 0 ug/L.

eFLOW (cfs)	uFLOW (cfs)	At Complete Mix % Eff.	At Complete Mix % Ups.	At Complete Mix WER	HCME (ug/L)	hWER
10	40	20.0	80.0	8.800	80.00	8.800
10	63	13.7	86.3	6.343	80.00	8.800
10	90	10.0	90.0	4.900	80.00	8.800
10	190	5.0	95.0	2.950	80.00	8.800
10	490	2.0	98.0	1.780	80.00	8.800
10	990	1.0	99.0	1.390	80.00	8.800
10	1990	0.5	99.5	1.195	80.00	8.800

All the WERs in this example are lower than the comparable WERs in the first example because the uWER dropped from 5 to 1; the limiting value of the WER at very high flow is 1. Also, the HCMEs and hWERs are independent of flow because the increased dilution does not allow any more metal to be discharged when uCONC = ussCCC, i.e., when the assimilative capacity is zero. As in the first example, any WER determined at a flow higher than design flow can be used as an environmentally conservative estimate of the design-flow WER and the hWERs show that the WER of 8.8 determined at design flow will provide adequate protection at all flows for which information is available. When uFLOW equals the design flow of 40 cfs, WER = hWER.

In the third example, uWER is assumed to be 2, which means that ussCCC = 4 ug/L. uCONC is assumed to be 1 ug/L; thus the assimilative capacity of the upstream water is 3 ug/L.

eFLOW (cfs)	uFLOW (cfs)	At Complete Mix % Eff.	At Complete Mix % Ups.	At Complete Mix WER	HCME (ug/L)	hWER
10	40	20.0	80.0	9.600	92.0	9.60
10	63	13.7	86.3	7.206	98.9	10.29
10	90	10.0	90.0	5.800	107.0	11.10
10	190	5.0	95.0	3.900	137.0	14.10
10	490	2.0	98.0	2.760	227.0	23.10
10	990	1.0	99.0	2.380	377.0	38.10
10	1990	0.5	99.5	2.190	677.0	68.10

All the WERs in this example are intermediate between the comparable WERs in the first two examples because the uWER is now 2, which is between 1 and 5; the limiting value of the WER at very high flow is 2. As in the other examples, any WER determined at a flow higher than design flow can be used as an environmentally conservative estimate of the design-flow WER and the hWERs show that the WER of 9.6 determined at design flow will provide adequate protection at all flows for which information is available. When uFLOW equals the design flow of 40 cfs, WER = hWER.

If this third example is assumed to be subject to acidic snowmelt in the spring so that the eWER and uWER are less-than-additive and result in a WER of 4.8 (rather than 5.8) at a uFLOW of 90 cfs, the <u>third</u> HCME would be 87 ug/L, and the third hWER would be 9.1. This hWER is lower than the design-flow WER of 9.6, so the site-specific criterion would have to be derived using the WER of 9.1, rather than the design-flow WER of 9.6, in order to provide the intended level of protection. If the eWER and uWER were less-than-additive only to the extent that the third WER was 5.3, the third HCME would be 97 ug/L and the third hWER would be 10.1. In this case, dilution by the increased flow would more than compensate for the WERs being less-than-additive, so that the design-flow WER of 9.6 would provide adequate protection at a uFLOW of 90 cfs. Auxiliary information might indicate whether an unusual WER is real or is an accident; for example, if the hardness, alkalinity, and pH of snowmelt are all low, this information would support a low WER.

If the eWER and uWER were more-than-additive so that the third WER was 10, this WER would not be an environmentally conservative estimate of the design-flow WER. If a WER determined at a higher flow is to be used as an estimate of the design-flow WER and there is reason to believe that the eWER and the uWER might be more-than-additive, a test for additivity can be performed (see Appendix G).

Calculating HCMEs and hWERs is straightforward if the WERs are based on the total recoverable measurement. If they are based on the dissolved measurement, it is necessary to take into account the percent of the total recoverable metal in the effluent that becomes dissolved in the downstream water.

To ensure adequate protection, a group of WERs should include one or more WERs corresponding to flows near the design flow, as well as one or more WERs corresponding to higher flows.

a. Calculation of hWERs from WERs determined at various flows and seasons identifies the highest WER that can be used in the derivation of a site-specific criterion and still provide adequate protection at all flows for which WERs are available. Use of hWERs eliminates the need to assume that WERs determined at design flow will provide adequate protection at higher flows. Because hWERs are calculated to apply at design flow, they apply to the flow on which the permit limits are based. The lowest of the hWERs ensures adequate protection at all flows, if hWERs are available for a sufficient range of flows, seasons, and other conditions.

b. Unless additivity is assumed, a WER cannot be extrapolated from one flow to another and therefore it is not possible to predict a design-flow WER from a WER determined at other conditions. The largest WER is likely to occur at design flow because, of the flows during which protection is to be provided, the design flow is the flow at which the highest concentration of effluent will probably occur in the downstream water. This largest WER has to be experimentally determined; it cannot be predicted.

The examples also illustrate that if the concentration of metal in the upstream water is below the site-specific criterion for that water, in the limit of infinite dilution of the effluent with upstream water, there will be adequate protection. The concern, therefore, is for intermediate levels of dilution. Even if the assimilative capacity is zero, as in the second example, there is more concern at the lower or intermediate flows, when the effluent load is still a major portion of the total load, than at higher flows when the effluent load is a minor contribution.

The Options

To ensure adequate protection over a range of flows, two types of WERs need to be determined:

Type 1 WERs are determined by obtaining samples of effluent and upstream water when the downstream flow is between one and two times higher than what it would be under design-flow conditions.

Type 2 WERs are determined by obtaining samples of effluent and upstream water when the downstream flow is between two and ten times higher than what it would be under design-flow conditions.

The only difference between the two types of samples is the downstream flow at the time the samples are taken. For both types of WERs, the samples should be mixed at the ratio of the flows that existed when the samples were taken so that seasonal and flow-related changes in the water quality characteristics of the upstream water are properly related to the flow at which they occurred. The ratio at which the samples are mixed does not have to be the exact ratio that existed when the samples were taken, but the ratio has to be known, which is why simulated downstream water is used. For each Type 1 WER and each Type 2 WER that is determined, a hWER is calculated.

Ideally, sufficient numbers of both types of WERs would be available and each WER would be sufficiently precise and accurate and the Type 1 WERs would be sufficiently similar that the FWER could be the geometric mean of the Type 1 WERs, unless the FWER had to be lowered because of one or more hWERs. If an adequate number of one or both types of WERs is not available, an environmentally conservative WER or hWER should be used as the FWER.

Three Type 1 and/or Type 2 WERs, which were determined using acceptable procedures and for which there were at least three weeks between any two sampling events, **must** be available in order for a FWER to be derived. If three or more are available, the FWER should be derived from the WERs and hWERs using the lowest numbered option whose requirements are satisfied:

1. If there are two or more Type 1 WERs:
   a. If at least nineteen percent of all of the WERs are Type 2 WERs, the derivation of the FWER depends on the properties of the Type 1 WERs:
      1) If the range of the Type 1 WERs is not greater than a factor of 5 and/or the range of the ratios of the Type 1 WER to the concentration of metal in the simulated downstream water is not greater than a factor of 5, the FWER is the lower of (a) the adjusted geometric mean (see Figure 2) of all of the Type 1 WERs and (b) the lowest hWER.
      2) If the range of the Type 1 WERs is greater than a factor of 5 and the range of the ratios of the Type 1 WER to the concentration of metal in the simulated downstream water is greater than a factor of 5, the FWER is the lowest of (a) the lowest Type 1 WER, (b) the lowest hWER, and (c) the geometric mean of all the Type 1 and Type 2 WERs, unless an analysis of the joint probabilities of the occurrences of WERs and metal concentrations indicates that a higher WER would still provide the level of protection intended by the criterion. (EPA intends to provide guidance concerning such an analysis.)
   b. If less than nineteen percent of all of the WERs are Type 2 WERs, the FWER is the lower of (1) the lowest Type 1 WER and (2) the lowest hWER.
2. If there is one Type 1 WER, the FWER is the lowest of (a) the Type 1 WER, (b) the lowest hWER, and (c) the geometric mean of all of the Type 1 and Type 2 WERs.
3. If there are no Type 1 WERs, the FWER is the lower of (a) the lowest Type 2 WER and (b) the lowest hWER.

If fewer than three WERs are available and a site-specific criterion is to be derived using a WER or a FWER, the WER or FWER has to be assumed to be 1. Examples of deriving FWERs using these options are presented in Figure 3.

The options are designed to ensure that:

a. The options apply equally well to ordinary flowing waters and to streams whose design flow is zero.
b. The requirements for deriving the FWER as something other than the lowest WER are not too stringent.
c. The probability is high that the criterion will be adequately protective at all flows, regardless of the amount of data that are available.
d. The generation of both types of WERs is encouraged because environmental conservatism is built in if both types of WERs are not available in acceptable numbers.
e. The amount of conservatism decreases as the quality and quantity of the available data increase.

The requirement that three WERs be available is based on a judgment that fewer WERs will not provide sufficient information. The requirement that at least nineteen percent of all of the available WERs be Type 2 WERs is based on a judgment concerning what constitutes an adequate mix of the two types of WERs: when there are five or more WERs, at least one-fifth should be Type 2 WERs.

Because each of these options for deriving a FWER is expected to provide adequate protection, anyone who desires to determine a FWER can generate three or more appropriate WERs and use the option that corresponds to the WERs that are available. The options that utilize the least useful WERs are expected to provide adequate protection because of the way the FWER is derived from the WERs. It is intended that, on the average, Option 1a will result in the highest FWER, and so it is recommended that data generation should be designed to satisfy the requirements of this option if possible. For example, if two Type 1 WERs have been determined, determining a third Type 1 WER will require use of Option 1b, whereas determining a Type 2 WER will require use of Option 1a.

Calculation of the FWER as an adjusted geometric mean raises three issues:

a. The level of protection would be greater if the lowest WER, rather than an adjusted mean, were used as the FWER. Although true, the intended level of protection is provided by the national aquatic life criterion derived according to the national guidelines; when sufficient data are available and it is clear how the data should be used, there is no reason to add a substantial margin of safety and thereby change the intended level of protection. Use of an adjusted geometric mean is acceptable if sufficient data are available concerning the WER to demonstrate that the adjusted geometric mean will provide the intended level of protection. Use of the lowest of three or more WERs would be justified, if, for example, the criterion had been lowered to protect a commercially important species and a WER determined with that species was lower than WERs determined with other species.

b. The level of protection would be greater if the adjustment was to a probability of 0.95 rather than to a probability of 0.70. As above, the intended level of protection is provided by the national aquatic life criterion derived according to the national guidelines. There is no need to substantially increase the level of protection when site-specific criteria are derived.

c. It would be easier to use the more common arithmetic mean, especially because the geometric mean usually does not provide much more protection than the arithmetic mean. Although true, use of the geometric mean rather than the arithmetic mean is justified on the basis of statistics and mathematics; use of the geometric mean is also consistent with the intended level of protection. Use of the arithmetic mean is appropriate when the values can range from minus infinity to plus infinity. The geometric mean (GM) is equivalent to using the arithmetic mean of the logarithms of the values. WERs cannot be negative, but the logarithms of WERs can. The distribution of the logarithms of WERs is therefore more likely to be normally distributed than is the distribution of the WERs. Thus, it is better to use the GM of WERs. In addition, when dealing with quotients, use of the GM reduces arguments about the correct way to do some calculations because the same answer is obtained in different ways. For example, if WER1 = (N1)/(D1) and WER2 = (N2)/(D2), then the GM of WER1 and WER2 gives the same value as [(GM of N1 and N2)/(GM of D1 and D2)] and also equals the square root of {[(N1)(N2)]/[(D1)(D2)]}.

Anytime the FWER is derived as the lowest of a series of experimentally determined WERs and/or hWERs, the magnitude of the FWER will depend at least in part on experimental variation. There are at least three ways that the influence of experimental variation on the FWER can be reduced:

a. A WER determined with a primary test can be replicated and the geometric mean of the replicates used as the value of the WER for that determination. Then the FWER would be the lowest of a number of geometric means rather than the lowest of a number of individual WERs. To be true replicates, the replicate determinations of a WER should not be based on the same test in laboratory dilution water, the same sample of site water, or the same sample of effluent.

b. If, for example, Option 3 is to be used with three Type 2 WERs and the endpoints of both the primary and secondary tests in laboratory dilution water are above the CMC and/or CCC to which the WER is to apply, WERs can be determined with both the primary and secondary tests for each of the three sampling times. For each sampling time, the geometric mean of the WER obtained with the primary test and the WER obtained with the secondary test could be calculated; then the lowest of these three geometric means could be used as the FWER. The three WERs cannot consist of some WERs determined with one of the tests and some WERs determined with the other test; similarly the three WERs cannot consist of a combination of individual WERs obtained with the primary and/or secondary tests and geometric means of results of primary and secondary tests.

c. As mentioned above, because the variability of the effluent might contribute substantially to the variability of the WERs, it might be desirable to obtain and store more than one sample of the effluent when a WER is to be determined in case an unusual WER is obtained with the first sample used.

Examples of the first and second ways of reducing the impact of experimental variation are presented in Figure 4. The availability of these alternatives does not mean that they are necessarily cost-effective.

6. For metals whose criteria are hardness-dependent, at what hardness should WERs be determined?

The issue of hardness bears on such topics as acclimation of test organisms to the site water, adjustment of the hardness of the site water, and how an experimentally determined WER should be used. If all WERs were determined at design-flow conditions, it might seem that all WERs should be determined at the design-flow hardness. Some permit limits, however, are not based on the hardness that is most likely to occur at design flow; in addition, conducting all tests at design-flow conditions provides no information concerning whether adequate protection will be provided at other flows. Thus, unless the hardnesses of the upstream water and the effluent are similar and do not vary with flow, the hardness of the site water will not be the same for all WER determinations.

Because the toxicity tests should be begun within 36 hours after the samples of effluent and upstream water are collected, there is little time to acclimate organisms to a sample-specific hardness. One alternative would be to acclimate the organisms to a preselected hardness and then adjust the hardness of the site water, but adjusting the hardness of the site water might have various effects on the toxicity of the metal due to competitive binding and ionic impacts on the test organisms and on the speciation of the metal; lowering hardness without also diluting the WER is especially problematic. The least objectionable approach is to acclimate the organisms to a laboratory dilution water with a hardness in the range of 50 to 150 mg/L and then use this water as the laboratory dilution water when the WER is determined. In this way, the test organisms will be acclimated to the laboratory dilution water as specified by ASTM (1993a,b,c,d,e).

Test organisms may be acclimated to the site water for a short time as long as this does not cause the tests to begin more than 36 hours after the samples were collected. Regardless of what acclimation procedure is used, the organisms used for the toxicity test conducted using site water are unlikely to be acclimated as well as would be desirable. This is a general problem with toxicity tests conducted in site water (U.S. EPA 1993a,b,c; ASTM 1993f), and its impact on the results of tests is unknown.

For the practical reasons given above, an experimentally determined WER will usually be a ratio of endpoints determined at two different hardnesses and will thus include contributions from a variety of differences between the two waters, including hardness. The disadvantages of differing hardnesses are that (a) the test organisms probably will not be adequately acclimated to site water and (b) additional calculations will be needed to account for the differing hardnesses; the advantages are that it allows the generation of data concerning the adequacy of protection at various flows of upstream water and it provides a way of overcoming two problems with the hardness equations: (1) it is not known how applicable they are to hardnesses outside the range of 25 to 400 mg/L and (2) it is not known how applicable they are to unusual combinations of hardness, alkalinity, and pH or to unusual ratios of calcium and magnesium.

The additional calculations that are necessary to account for the differing hardnesses will also overcome the shortcomings of the hardness equations. The purpose of determining a WER is to determine how much metal can be in a site water without lowering the intended level of protection. Each experimentally determined WER is inherently referenced to the hardness of the laboratory dilution water that was used in the determination of the WER, but the hardness equation can be used to calculate adjusted WERs that are referenced to other hardnesses for the laboratory dilution water. When used to adjust WERs, a hardness equation for a CMC or CCC can be used to reference a WER to any hardness for a laboratory dilution water, whether it is inside or outside the range of 25 to 400 mg/L, because any inappropriateness in the equation will be automatically compensated for when the adjusted WER is used in the derivation of a FWER and permit limits.

For example, the hardness equation for the freshwater CMC for copper gives CMCs of 9.2, 18, and 34 ug/L at hardnesses of 50, 100, and 200 mg/L, respectively. If acute toxicity tests with Ceriodaphnia reticulata gave an EC50 of 18 ug/L using a laboratory dilution water with a hardness of 100 mg/L and an EC50 of 532.2 ug/L in a site water, the resulting WER would be 29.57. It can be assumed that, within experimental variation, EC50s of 9.2 and 34 ug/L and WERs of 57.85 and 15.65 would have been obtained if laboratory dilution waters with hardnesses of 50 and 200 mg/L, respectively, had been used, because the EC50 of 532.2 ug/L obtained in the site water does not depend on what water is used for the laboratory dilution water. The WERs of 57.85 and 15.65 can be considered to be adjusted WERs that were extrapolated from the experimentally determined WER using the hardness equation for the copper CMC. If used correctly, the experimentally determined WER and all of the adjusted WERs will result in the same permit limits because they are internally consistent and are all based on the EC50 of 532.2 ug/L that was obtained in site water.

A hardness equation for copper can be used to adjust the WER if the hardness of the laboratory dilution water used in the determination of the WER is in the range of 25 to 400 mg/L (preferably in the range of about 40 to 250 mg/L because most of the data used to derive the equation are in this range). However, the hardness equation can be used to adjust WERs to hardnesses outside the range of 25 to 400 mg/L because the basis of the adjusted WER does not change the fact that the EC50 obtained in site water was 532.2 ug/L. If the hardness of the site water was 16 mg/L, the hardness equation would predict an EC50 of 3.153 ug/L, which would result in an adjusted WER of 168.8. This use of the hardness equation outside the range of 25 to 400 mg/L is valid only if the calculated CMC is used with the corresponding adjusted WER. Similarly, if the hardness of the site water had been 447 mg/L, the hardness equation would predict an EC50 of 72.66 ug/L, with a corresponding adjusted WER of 7.325. If the hardness of 447 mg/L were due to an effluent that contained calcium chloride and the alkalinity and pH of the site water were what would usually occur at a hardness of 50 mg/L rather than 400 mg/L, any inappropriateness in the calculated EC50 of 72.66 ug/L will be compensated for in the adjusted WER of 7.325, because the adjusted WER is based on the EC50 of 532.2 ug/L that was obtained using the site water.

In the above examples it was assumed that at a hardness of 100 mg/L the EC50 for C. reticulata equalled the CMC, which is a very reasonable simplifying assumption. If, however, the WER had been determined with the more resistant Daphnia pulex and EC50s of 50 ug/L and 750 ug/L had been obtained using a laboratory dilution water and a site water, respectively, the CMC given by the hardness equation could not be used as the predicted EC50. A new equation would have to be derived by changing the intercept so that the new equation gives an EC50 of 50 ug/L at a hardness of 100 mg/L; this new equation could then be used to calculate adjusted EC50s, which could then be used to calculate corresponding adjusted WERs:

Hardness (mg/L)	EC50 (ug/L)	WER
16	8.894	84.33
50	26.022	28.82
100	50.000*	15.00*
200	96.073	7.81
447	204.970	3.66

The values marked with an asterisk are the assumed experimentally determined values; the others were calculated from these values. At each hardness the product of the EC50 times the WER equals 750 ug/L because all of the WERs are based on the same EC50 obtained using site water. Thus use of the WER allows application of the hardness equation for a metal to conditions to which it otherwise might not be applicable.

<u>HCMEs can then be calculated using either the experimentally determined WER or an adjusted WER as long as the WER is applied to the CMC that corresponds to the hardness on which the WER is based.</u> For example, if the concentration of copper in the upstream water was 1 ug/L and the flows of the effluent and upstream water were 9 and 73 cfs, respectively, when the samples were collected, the HCME calculated from the WER of 15.00 would be:

$$HCME = \frac{(17.73\ ug/L)(15)(9 + 73\ cfs) - (1\ ug/L)(73\ cfs)}{9\ cfs} = 2415\ ug/L$$

because the CMC is 17.73 ug/L at a hardness of 100 mg/L. (The value of 17.73 ug/L is used for the CMC instead of 18 ug/L to reduce roundoff error in this example.) If the hardness of the site water was actually 447 ug/L, the HCME could also be calculated using the WER of 3.66 and the CMC of 72.66 ug/L that would be obtained from the CMC hardness equation:

$$HCME = \frac{(72.66\ ug/L)(3.66)(9 + 73\ cfs) - (1\ ug/L)(73\ cfs)}{9\ cfs} = 2415\ ug/L\ .$$

Either WER can be used in the calculation of the HCME as long as the CMC and the WER correspond to the same hardness and therefore to each other, because:

$$(17.73\ ug/L)(15) = (72.66\ ug/L)(3.66)\ .$$

Although the HCME will be correct as long as the hardness, CMC, and WER correspond to each other, the WER used in the derivation of the FWER **must** be the one that is calculated using a hardness equation to be compatible with the hardness of the site water. If the hardness of the site water was 447 ug/L, the WER used in the derivation of the FWER has to be 3.66; therefore, the simplest approach is to calculate the HCME using the WER of 3.66 and the corresponding CMC of 72.66 ug/L, because these correspond to the hardness of 447 ug/L, which is the hardness of the site water.

In contrast, the hWER should be calculated using the CMC that corresponds to the design hardness. If the design hardness is 50 mg/L, the corresponding CMC is 9.2 ug/L. If the design flows of the effluent and the upstream water are 9 and 20 cfs, respectively, and the concentration of metal in upstream water at design conditions is 1 ug/L, the hWER obtained from the WER determined using the site water with a hardness of 447 mg/L would be:

$$hWER = \frac{(2415\ ug/L)(9\ cfs) + (1\ ug/L)(20\ cfs)}{(9.2\ ug/L)(9\ cfs + 20\ cfs)} = 81.54\ .$$

None of these calculations provides a way of extrapolating a WER from one site-water hardness to another. The only extrapolations that are possible are from one hardness of laboratory dilution water to another; the adjusted WERs are based on predicted toxicity in laboratory dilution water, but they are all based on measured toxicity in site water. If a WER is to apply to the design flow and the design hardness, one or more toxicity tests have to be conducted using samples of effluent and upstream water obtained under design-flow conditions and mixed at the design-flow ratio to produce the design hardness. A WER that is specifically appropriate to design conditions cannot be based on predicted toxicity in site water; it has to be based on measured toxicity in site water that corresponds to design-flow conditions. The situation is more complicated if the design hardness is not the hardness that is most likely to occur when effluent and upstream water are mixed at the ratio of the design flows.

B. Background Information and Initial Decisions

1. Information should be obtained concerning the effluent and the operating and discharge schedules of the discharger.

2. The spatial extent of the site to which the WER and the site-specific criterion are intended to apply should be defined (see Appendix A). Information concerning tributaries, the plume, and the point of complete mix should be obtained. Dilution models (U.S. EPA 1993d) and dye dispersion studies (Kilpatrick 1992) might provide information that is useful for defining sites for cmcWERs.

3. If the Recalculation Procedure (see Appendix B) is to be used, it should be performed.

4. Pertinent information concerning the calculation of the permit limits should be obtained:
   a. What are the design flows, i.e., the flow of the upstream water (e.g., 7Q10) and the flow of the effluent that are used in the calculation of the permit limits? (The design flows for the CMC and CCC might be the same or different.)
   b. Is there a CMC (acute) mixing zone and/or a CCC (chronic) mixing zone?
   c. What are the dilution(s) at the edge(s) of the mixing zone(s)?
   d. If the criterion is hardness-dependent, what is the hardness on which the permit limits are based? Is this a hardness that is likely to occur under design-flow conditions?

5. It should be decided whether to determine a cmcWER and/or a cccWER.

6. The water quality criteria document (see Appendix E) that serves as the basis of the aquatic life criterion should be read to identify any chemical or toxicological properties of the metal that are relevant.

7. If the WER is being determined by or for a discharger, it will probably be desirable to decide what is the smallest WER that is desired by the discharger (e.g., the smallest WER that would not require a reduction in the amount of metal discharged). This "smallest desired WER" might be useful when deciding whether to determine a WER. If a WER is determined, this "smallest desired WER" might be useful when selecting the range of concentrations to be tested in the site water.

8. Information should be read concerning health and safety considerations regarding collection and handling of

effluent and surface water samples and conducting toxicity tests (U.S. EPA 1993a; ASTM 1993a). Information should also be read concerning safety and handling of the metallic salt that will be used in the preparation of the stock solution.

9. The proposed work should be discussed with the appropriate regulatory authority (and possibly the Water Management Division of the EPA Regional Office) before deciding how to proceed with the development of a detailed workplan.

10. Plans should be made to perform one or more rangefinding tests in both laboratory dilution water and site water (see section G.7).

C. Selecting Primary and Secondary Tests

1. For each WER (cmcWER and/or cccWER) to be determined, the primary and secondary tests should be selected using the rationale presented in section A.3, the information in Appendix I, the information in the criteria document for the metal (see Appendix E), and any other pertinent information that is available. When a specific test species is not specified, also select the species. Because at least three WERs **must** be determined with the primary test, but only one **must** be determined with the secondary test, selection of the tests might be influenced by the availability of the species (and the life stage in some cases) during the planned testing period.
    a. The description of a "test" specifies not only the test species and the duration of the test but also the life stage of the species and the adverse effect on which the results are to be based, all of which can have a major impact on the sensitivity of the test.
    b. The endpoint (e.g., LC50, EC50, IC50) of the primary test in laboratory dilution water should be as close as possible, but it **must not** be below, the CMC and/or CCC to which the WER is to be applied, because for any two tests, the test that has the lower endpoint is likely to give the higher WER (see Appendix D).
    NOTE: If both the Recalculation Procedure and a WER are to be used in the derivation of the site-specific criterion, the Recalculation Procedure **must** be completed first because the recalculated CMC and/or CCC **must** be used in the selection of the primary and secondary tests.
    c. The endpoint (e.g., LC50, EC50, IC50) of the secondary test in laboratory dilution water should be as close as possible, but may be above or below, the CMC and/or CCC to which the WER is to be applied.

1) Because few toxicity tests have endpoints close to the CMC and CCC and because the major use of the secondary test is confirmation (see section I.7.b), the endpoint of the secondary test may be below the CMC or CCC. If the endpoint of the secondary test in laboratory dilution water is above the CMC and/or CCC, it might be possible to use the results to reduce the impact of experimental variation (see Figure 4). If the endpoint of the primary test in laboratory dilution water is above the CMC and the endpoint of the secondary test is between the CMC and CCC, it should be possible to determine both a cccWER and a cmcWER using the same two tests.
2) It is often desirable to conduct the secondary test when the first primary test is conducted in case the results are surprising; conducting both tests the first time also makes it possible to interchange the primary and secondary tests, if desired, without increasing the number of tests that need to be conducted. (If results of one or more rangefinding tests are not available, it might be desirable to wait and conduct the secondary test when more information is available concerning the laboratory dilution water and the site water.)

2. The primary and secondary tests **must** be conducted with species in different taxonomic <u>orders</u>; at least one species **must** be an animal and, when feasible, one species should be a vertebrate and the other should be an invertebrate. A plant cannot be used if nutrients and/or chelators need to be added to either or both dilution waters in order to determine the WER. It is desirable to use a test and species for which the rate of success is known to be high and for which the test organisms are readily available. (If the WER is to be used with a recalculated CMC and/or CCC, the species used in the primary and secondary tests do <u>not</u> have to be on the list of species that are used to obtain the recalculated CMC and/or CCC.)

3. There are advantages to using tests suggested in Appendix I or other tests of comparable sensitivity for which data are available from one or more other laboratories.
   a. A good indication of the sensitivity of the test is available. This helps ensure that the endpoint in laboratory dilution water is close to the CMC and/or CCC and aids in the selection of concentrations of the metal to be used in the rangefinding and/or definitive toxicity tests in laboratory dilution water. Tests with other species such as species that occur at the site may be used, but it is sometimes more difficult to obtain, hold, and test such species.

b. When a WER is determined and used, the results of the tests in laboratory dilution water provide the connection between the data used in the derivation of the national criterion and the data obtained in site water, i.e., the results in laboratory dilution water are a vital link in the derivation and use of a WER. It is, therefore, important to be able to judge the quality of the results in laboratory dilution water. Comparison of results with data from other laboratories evaluates all aspects of the test methodology simultaneously, but for the determination of WERs, the most important aspect is the quality of the laboratory dilution water because the dilution water is the most important difference between the two side-by-side tests from which the WER is calculated. Thus, two tests **must** be conducted for which data are available on the metal of concern in a laboratory dilution water from at least one other laboratory. If both the primary and secondary tests are ones for which acceptable data are available from at least one other laboratory, these are the only two tests that have to be conducted. If, however, the primary and/or secondary tests are ones for which no results are already available for the metal of concern from another laboratory, the first or second time a WER is determined at least two additional tests **must** be conducted in the laboratory dilution water in addition to the tests that are conducted for the determination of WERs (see sections F.5 and I.5).

1) For the determination of a WER, data are not required for a reference toxicant with either the primary test or the secondary test because the above requirement provides similar data for the metal for which the WER is actually being determined.
2) See Section I.5 concerning interpretation of the results of these tests before additional tests are conducted.

D. Acquiring and Acclimating Test Organisms

1. The test organisms should be obtained, cultured, held, acclimated, fed, and handled as recommended by the U.S. EPA (1993a,b,c) and/or by ASTM (1993a,b,c,d,e). All test organisms **must** be acceptably acclimated to a laboratory dilution water that satisfies the requirements given in sections F.3 and F.4; an appropriate number of the organisms may be randomly or impartially removed from the laboratory dilution water and placed in the site water when it becomes available in order to acclimate the organisms to the site water for a while just before the tests are begun.

2. The organisms used in a pair of side-by-side tests **must** be drawn from the same population and tested under identical conditions.

E. Collecting and Handling Upstream Water and Effluent

1. Upstream water will usually be mixed with effluent to prepare simulated downstream water. Upstream water may also be used as a site water if a WER is to be determined using upstream water in addition to or instead of determining a WER using downstream water. The samples of upstream water **must** be representative; they **must not** be unduly affected by recent runoff events (or other erosion or resuspension events) that cause higher levels of TSS than would normally be present, unless there is particular concern about such conditions.

2. The sample of effluent used in the determination of a WER **must** be representative; it **must** be collected during a period when the discharger is operating normally. Selection of the date and time of sampling of the effluent should take into account the discharge pattern of the discharger. It might be appropriate to collect effluent samples during the middle of the week to allow for reestablishment of steady-state conditions after shutdowns for weekends and holidays; alternatively, if end-of-the-week slug discharges are routine, they should probably be evaluated. As mentioned above, because the variability of the effluent might contribute substantially to the variability of the WERs, it might be desirable to obtain and store more than one sample of the effluent when WERs are to be determined in case an unusual WER is obtained with the first sample used.

3. When samples of site water and effluent are collected for the determination of the WERs with the primary test, there **must** be <u>at least three weeks</u> between one sampling event and the next. It is desirable to obtain samples in at least two different seasons and/or during times of probable differences in the characteristics of the site water and/or effluent.

4. Samples of upstream water and effluent **must** be collected, transported, handled, and stored as recommended by the U.S. EPA (1993a). For example, samples of effluent should usually be composites, but grab samples are acceptable if the residence time of the effluent is sufficiently long. A sufficient volume should be obtained so that some can be stored for additional testing or analyses if an unusual WER is obtained. Samples **must** be stored at 0 to 4°C in the dark with no air space in the sample container.

5. At the time of collection, the flow of both the upstream water and the effluent **must** be either measured or estimated by means of correlation with a nearby U.S.G.S. gauge, the pH of both upstream water and effluent **must** be measured, and samples of both upstream water and effluent should be filtered for measurement of dissolved metals. Hardness, TSS, TOC, and total recoverable and dissolved metal **must** be measured in both the effluent and the upstream water. Any other water quality characteristics, such as total dissolved solids (TDS) and conductivity, that are monitored monthly or more often by the permittee and reported in the Discharge Monitoring Report **must** also be measured. These and the other measurements provide information concerning the representativeness of the samples and the variability of the upstream water and effluent.

6. "Chain of custody" procedures (U.S. EPA 1991b) should be used for all samples of site water and effluent, especially if the data might be involved in a legal proceeding.

7. Tests **must** be begun within 36 hours after the collection of the samples of the effluent and/or the site water, except that tests may be begun more than 36 hours after the collection of the samples if it would require an inordinate amount of resources to transport the samples to the laboratory and begin the tests within 36 hours.

8. If acute and/or chronic tests are to be conducted with daphnids and if the sample of the site water contains predators, the site water **must** be filtered through a 37-μm sieve or screen to remove predators.

F. Laboratory Dilution Water

1. The laboratory dilution water **must** satisfy the requirements given by U.S. EPA (1993a,b,c) or ASTM (1993a,b,c,d,e). The laboratory dilution water **must** be a ground water, surface water, reconstituted water, diluted mineral water, or dechlorinated tap water that has been demonstrated to be acceptable to aquatic organisms. If a surface water is used for acute or chronic tests with daphnids and if predators are observed in the sample of the water, it **must** be filtered through a 37-μm sieve or screen to remove the predators. Water prepared by such treatments as deionization and reverse osmosis **must not** be used as the laboratory dilution water unless salts, mineral water, hypersaline brine, or sea salts are added as recommended by U.S. EPA (1993a) or ASTM (1993a).

2. The concentrations of both TOC and TSS **must** be less than 5 mg/L.

3. The hardness of the laboratory dilution water should be between 50 and 150 mg/L and **must** be between 40 and 220 mg/L. If the criterion for the metal is hardness-dependent, the hardness of the laboratory dilution water **must not** be above the hardness of the site water, unless the hardness of the site water is below 50 mg/L.

4. The alkalinity and pH of the laboratory dilution water **must** be appropriate for its hardness; values for alkalinity and pH that are appropriate for some hardnesses are given by U.S. EPA (1993a) and ASTM (1993a); other corresponding values should be determined by interpolation. Alkalinity should be adjusted using sodium bicarbonate, and pH should be adjusted using aeration, sodium hydroxide, and/or sulfuric acid.

5. It would seem reasonable that, before any samples of site water or effluent are collected, the toxicity tests that are to be conducted in the laboratory dilution water for comparison with results of the same tests from other laboratories (see sections C.3.b and I.5) should be conducted. These should be performed at the hardness, alkalinity, and pH specified in sections F.3 and F.4.

G. Conducting Tests

1. There **must** be no differences between the side-by-side tests other than the composition of the dilution water, the concentrations of metal tested, and possibly the water in which the test organisms are acclimated just prior to the beginning of the tests.

2. More than one test using site water may be conducted side-by-side with a test using laboratory dilution water; the one test in laboratory dilution water will be used in the calculation of several WERs, which means that it is very important that that one test be acceptable.

3. Facilities for conducting toxicity tests should be set up and test chambers should be selected and cleaned as recommended by the U.S. EPA (1993a,b,c) and/or ASTM (1993a,b,c,d,e).

4. A stock solution should be prepared using an inorganic salt that is highly soluble in water.
   a. The salt does not have to be one that was used in tests that were used in the derivation of the national criterion. Nitrate salts are generally acceptable;

chloride and sulfate salts of many metals are also acceptable (see Appendix J). It is usually desirable to avoid use of a hygroscopic salt. The salt used should meet A.C.S. specifications for reagent-grade, if such specifications are available; use of a better grade is usually not worth the extra cost. No salt should be used until information concerning safety and handling has been read.

b. The stock solution may be acidified (using metal-free nitric acid) only as necessary to get the metal into solution.

c. The same stock solution **must** be used to add metal to all tests conducted at one time.

5. For tests suggested in Appendix I, the appendix presents the recommended duration and whether the static or renewal technique should be used; additional information is available in the references cited in the appendix. Regardless of whether or not or how often test solutions are renewed when these tests are conducted for other purposes, the following guidance applies to all tests that are conducted for the determination of WERs:
   a. The renewal technique **must** be used for tests that last longer than 48 hr.
   b. If the concentration of dissolved metal decreases by more than 50 % in 48 hours in static or renewal tests, the test solutions **must** be renewed every 24 hours. Similarly, if the concentration of dissolved oxygen becomes too low, the test solutions **must** be renewed every 24 hours. If one test in a pair of tests is a renewal test, both tests **must** be renewal tests.
   c. When test solutions are to be renewed, the new test solutions **must** be prepared from the original unspiked effluent and water samples that have been stored at 0 to 4°C in the dark with no air space in the sample container.
   d. The static technique may be used for tests that do not last longer than 48 hours unless the above specifications require use of the renewal technique.

   If a test is used that is not suggested in Appendix I, the duration and technique recommended for a comparable test should be used.

6. Recommendations concerning temperature, loading, feeding, dissolved oxygen, aeration, disturbance, and controls given by the U.S. EPA (1993a,b,c) and/or ASTM (1993a,b,c,d,e) **must** be followed. The procedures that are used **must** be used in both of the side-by-side tests.

7. To aid in the selection of the concentrations of metals that should be used in the test solutions in site water, a static rangefinding test should be conducted for 8 to 96

hours, using a dilution factor of 10 (or 0.1) or 3.2 (or 0.32) increasing from about a factor of 10 below the value of the endpoint given in the criteria document for the metal or in Appendix I of this document for tests with newly hatched fathead minnows. If the test is not in the criteria document and no other data are available, a mean acute value or other data for a taxonomically similar species should be used as the predicted value. This rangefinding test will provide information concerning the concentrations that should be used to bracket the endpoint in the definitive test and will provide information concerning whether the control survival will be acceptable. If dissolved metal is measured in one or more treatments at the beginning and end of the rangefinding test, these data will indicate whether the concentration should be expected to decrease by more than 50 % during the definitive test. The rangefinding test may be conducted in either of two ways:

a. It may be conducted using the samples of effluent and site water that will be used in the definitive test. In this case, the duration of the rangefinding test should be as long as possible within the limitation that the definitive test **must** begin within 36 hours after the samples of effluent and/or site water were collected, except as per section E.7.
b. It may be conducted using one set of samples of effluent and upstream water with the definitive tests being conducted using samples obtained at a later date. In this case the rangefinding test might give better results because it can last longer, but there is the possibility that the quality of the effluent and/or site water might change. Chemical analyses for hardness and pH might indicate whether any major changes occurred from one sample to the next.

Rangefinding tests are especially desirable before the first set of toxicity tests. It might be desirable to conduct rangefinding tests before each individual determination of a WER to obtain additional information concerning the effluent, dilution water, organisms, etc., before each set of side-by-side tests are begun.

8. Several considerations are important in the selection of the dilution factor for definitive tests. Use of concentrations that are close together will reduce the uncertainty in the WER but will require more concentrations to cover a range within which the endpoints might occur. Because of the resources necessary to determine a WER, it is important that endpoints in both dilution waters be obtained whenever a set of side-by-side tests are conducted. Because static and renewal tests can be used to determine WERs, it is relatively easy to use more treatments than would be used in flow-through tests.

The dilution factor for total recoverable metal **must** be between 0.65 and 0.99, and the recommended factor is 0.7. Although factors between 0.75 and 0.99 may be used, their use will probably not be cost-effective. Because there is likely to be more uncertainty in the predicted value of the endpoint in site water, 6 or 7 concentrations are recommended in the laboratory dilution water, and 8 or 9 in the simulated downstream water, at a dilution factor of 0.7. It might be desirable to use even more treatments in the first of the WER determinations, because the design of subsequent tests can be based on the results of the first tests if the site water, laboratory dilution water, and test organisms do not change too much. The cost of adding treatments can be minimized if the concentration of metal is measured only in samples from treatments that will be used in the calculation of the endpoint.

9. Each test **must** contain a dilution-water control. The number of test organisms intended to be exposed to each treatment, including the controls, **must** be at least 20. It is desirable that the organisms be distributed between two or more test chambers per treatment. If test organisms are not randomly assigned to the test chambers, they **must** be assigned impartially (U.S. EPA 1993a; ASTM 1993a) between all test chambers for a pair of side-by-side tests. For example, it is not acceptable to assign 20 organisms to one treatment, and then assign 20 organisms to another treatment, etc. Similarly, it is not acceptable to assign all the organisms to the test using one of the dilution waters and then assign organisms to the test using the other dilution water. The test chambers should be assigned to location in a totally random arrangement or in a randomized block design.

10. For the test using site water, one of the following procedures should be used to prepare the test solutions for the test chambers and the "chemistry controls" (see section H.1):
    a. Thoroughly mix the sample of the effluent and place the same known volume of the effluent in each test chamber; add the necessary amount of metal, which will be different for each treatment; mix thoroughly; let stand for 2 to 4 hours; add the necessary amount of upstream water to each test chamber; mix thoroughly; let stand for 1 to 3 hours.
    b. Add the necessary amount of metal to a large sample of the effluent and also maintain an unspiked sample of the effluent; perform serial dilution using a graduated cylinder and the well-mixed spiked and unspiked samples of the effluent; let stand for 2 to 4 hours; add the necessary amount of upstream water to each test chamber; mix thoroughly; let stand for 1 to 3 hours.

c. Prepare a large volume of simulated downstream water by mixing effluent and upstream water in the desired ratio; place the same known volume of the simulated downstream water in each test chamber; add the necessary amount of metal, which will be different for each treatment; mix thoroughly and let stand for 1 to 3 hours.
d. Prepare a large volume of simulated downstream water by mixing effluent and upstream water in the desired ratio; divide it into two portions; prepare a large volume of the highest test concentration of metal using one portion of the simulated downstream water; perform serial dilution using a graduated cylinder and the well-mixed spiked and unspiked samples of the simulated downstream water; let stand for 1 to 3 hours.

Procedures "a" and "b" allow the metal to equilibrate somewhat with the effluent before the solution is diluted with upstream water.

11. For the test using the laboratory dilution water, either of the following procedures may be used to prepare the test solutions for the test chambers and the "chemistry controls" (see section H.1):
    a. Place the same known volume of the laboratory dilution water in each test chamber; add the necessary amount of metal, which will be different for each treatment; mix thoroughly; let stand for 1 to 3 hours.
    b. Prepare a large volume of the highest test concentration in the laboratory dilution water; perform serial dilution using a graduated cylinder and the well-mixed spiked and unspiked samples of the laboratory dilution water; let stand for 1 to 3 hours.

12. The test organisms, which have been acclimated as per section D.1, **must** be added to the test chambers for the site-by-side tests at the same time. The time at which the test organisms are placed in the test chambers is defined as the beginning of the tests, which **must** be within 36 hours of the collection of the samples, except as per section E.7.

13. Observe the test organisms and record the effects and symptoms as specified by the U.S. EPA (1993a,b,c) and/or ASTM (1993a,b,c,d,e). Especially note whether the effects, symptoms, and time course of toxicity are the same in the side-by-side tests.

14. Whenever solutions are renewed, sufficient solution should be prepared to allow for chemical analyses.

H. Chemical and Other Measurements

1. To reduce the possibility of contamination of test solutions before or during tests, thermometers and probes for measuring pH and dissolved oxygen **must not** be placed in test chambers that will provide data concerning effects on test organisms or data concerning the concentration of the metal. Thus measurements of pH, dissolved oxygen, and temperature before or during a test **must** be performed either on "chemistry controls" that contain test organisms and are fed the same as the other test chambers or on aliquots that are removed from the test chambers. The other measurements may be performed on the actual test solutions at the beginning and/or end of the test or the renewal.

2. Hardness (in fresh water) or salinity (in salt water), pH, alkalinity, TSS, and TOC **must** be measured on the upstream water, the effluent, the simulated and/or actual downstream water, and the laboratory dilution water. Measurement of conductivity and/or total dissolved solids (TDS) is recommended in fresh water.

3. Dissolved oxygen, pH, and temperature **must** be measured during the test at the times specified by the U.S. EPA (1993a,b,c) and/or ASTM (1993a,b,c,d,e). The measurements **must** be performed on the same schedule for both of the side-by-side tests. Measurements **must** be performed on both the chemistry controls and actual test solutions at the end of the test.

4. Both total recoverable and dissolved metal **must** be measured in the upstream water, the effluent, and appropriate test solutions for each of the tests.
   a. The analytical measurements should be sufficiently sensitive and precise that variability in analyses will not greatly increase the variability of the WERs. If the detection limit of the analytical method that will be used to determine the metal is greater than one-tenth of the CCC or CMC that is to be adjusted, the analytical method should probably be improved or replaced (see Appendix C). If additional sensitivity is needed, it is often useful to separate the metal from the matrix because this will simultaneously concentrate the metal and remove interferences. Replicate analyses should be performed if necessary to reduce the impact of analytical variability.
      1) EPA methods (U.S. EPA 1983b,1991c) should usually be used for both total recoverable and dissolved measurements, but in some cases alternate methods might have to be used in order to achieve the necessary sensitivity. Approval for use of

alternate methods is to be requested from the appropriate regulatory authority.

b. All measurements of metals **must** be performed using appropriate QA/QC techniques. <u>Clean techniques for obtaining, handling, storing, preparing, and analyzing the samples should be used when necessary to achieve blanks that are sufficiently low (see Appendix C).</u>

c. Rather than measuring the metal in all test solutions, it is often possible to store samples and then analyze only those that are needed to calculate the results of the toxicity tests. For dichotomous data (e.g., either-or data; data concerning survival), the metal in the following **must** be measured:
   1) all concentrations in which some, but not all, of the test organisms were adversely affected.
   2) the highest concentration that did not adversely affect any test organisms.
   3) the lowest concentration that adversely affected all of the test organisms.
   4) the controls.

   For data that are not dichotomous (i.e., for count and continuous data), the metal in the controls and in the treatments that define the concentration-effect curve **must** be measured; measurement of the concentrations of metals in other treatments is desirable.

d. In each treatment in which the concentration of metal is to be measured, <u>both the total recoverable and dissolved concentrations **must** be measured</u>:
   1) Samples **must** be taken for measurement of total recoverable metal once for a static test, and once for each renewal for renewal tests; in renewal tests, the samples are to be taken after the organisms have been transferred to the new test solutions. When total recoverable metal is measured in a test chamber, the whole solution in the chamber **must** be mixed before the sample is taken for analysis; the solution in the test chamber **must not** be acidified before the sample is taken. The sample **must** be acidified after it is placed in the sample container.
   2) Dissolved metal **must** be measured at the beginning and end of each static test; in a renewal test, the dissolved metal **must** be measured at the beginning of the test and just before the solution is renewed the first time. When dissolved metal is measured in a test chamber, the whole solution in the test chamber **must** be mixed before a sufficient amount is removed for filtration; the solution in the test chamber **must not** be acidified before the sample is taken. The sample **must** be filtered within one hour after it is taken, and the filtrate **must** be acidified after filtration.

5. Replicates, matrix spikes, and other QA/QC checks **must** be performed as required by the U.S. EPA (1983a,1991c).

I. Calculating and Interpreting the Results

1. To prevent roundoff error in subsequent calculations, at least four significant digits **must** be retained in all endpoints, WERs, and FWERs. This requirement is not based on mathematics or statistics and does not reflect the precision of the value; its purpose is to minimize concern about the effects of rounding off on a site-specific criterion. All of these numbers are intermediate values in the calculation of permit limits and should not be rounded off as if they were values of ultimate concern.

2. Evaluate the acceptability of each toxicity test individually.
   a. If the procedures used deviated from those specified above, particularly in terms of acclimation, randomization, temperature control, measurement of metal, and/or disease or disease-treatment, the test should be rejected; if deviations were numerous and/or substantial, the test **must** be rejected.
   b. Most tests are unacceptable if more than 10 percent of the organisms in the controls were adversely affected, but the limit is higher for some tests; for the tests recommended in Appendix I, the references given should be consulted.
   c. If an LC50 or EC50 is to be calculated:
      1) The percent of the organisms that were adversely affected **must** have been less than 50 percent, and should have been less than 37 percent, in at least one treatment other than the control.
      2) In laboratory dilution water the percent of the organisms that were adversely affected **must** have been greater than 50 percent, and should have been greater than 63 percent, in at least one treatment. In site water the percent of the organisms that were adversely affected should have been greater than 63 percent in at least one treatment. (The LC50 or EC50 may be a "greater than" or "less than" value in site water, but not in laboratory dilution water.)
      3) If there was an inversion in the data (i.e., if a lower concentration killed or affected a greater percentage of the organisms than a higher concentration), it **must not** have involved more than two concentrations that killed or affected between 20 and 80 percent of the test organisms.

   If an endpoint other than an LC50 or EC50 is used or if Abbott's formula is used, the above requirements will have to be modified accordingly.

d. Determine whether there was anything unusual about the test results that would make them questionable.
e. If solutions were not renewed every 24 hours, the concentration of dissolved metal **must not** have decreased by more than 50 percent from the beginning to the end of a static test or from the beginning to the end of a renewal in a renewal test in test concentrations that were used in the calculation of the results of the test.

3. Determine whether the effects, symptoms, and time course of toxicity was the same in the side-by-side tests in the site water and the laboratory dilution water. For example, did mortality occur in one acute test, but immobilization in the other? Did most deaths occur before 24 hours in one test, but after 24 hours in the other? In sublethal tests, was the most sensitive effect the same in both tests? If the effects, symptoms, and/or time course of toxicity were different, it might indicate that the test is questionable or that additivity, synergism, or antagonism occurred in site water. Such information might be particularly useful when comparing tests that produced unusually low or high WERs with tests that produced moderate WERs.

4. Calculate the results of each test:
   a. If the data for the most sensitive effect are dichotomous, the endpoint **must** be calculated as a LC50, EC50, LC25, EC25, etc., using methods described by the U.S. EPA (1993a) or ASTM (1993a). If two or more treatments affected between 0 and 100 percent in both tests in a side-by-side pair, probit analysis **must** be used to calculate results of both tests, unless the probit model is rejected by the goodness of fit test in one or both of the acute tests. If probit analysis cannot be used, either because fewer than two percentages are between 0 and 100 percent or because the model does not fit the data, computational interpolation **must** be used (see Figure 5); graphical interpolation **must not** be used.
      1) The same endpoint (LC50, EC25, etc.) and the same computational method **must** be used for both tests used in the calculation of a WER.
      2) The selection of the percentage used to define the endpoint might be influenced by the percent effect that occurred in the tests and the correspondence with the CCC and/or CMC.
      3) If no treatment killed or affected more than 50 percent of the test organisms and the test was otherwise acceptable, the LC50 or EC50 should be reported to be greater than the highest test concentration.

4) If no treatment other than the control killed or affected less than 50 percent of the test organisms and the test was otherwise acceptable, the LC50 or EC50 should be reported to be less than the lowest test concentration.

b. If the data for the most sensitive effect are not dichotomous, the endpoint **must** be calculated using a regression-type method (Hoekstra and Van Ewijk 1993; Stephan and Rogers 1985), such as linear interpolation (U.S. EPA 1993b,c) or a nonlinear regression method (Barnthouse et al. 1987; Suter et al. 1987; Bruce and Versteeg 1992). The selection of the percentage used to define the endpoint might be influenced by the percent effect that occurred in the tests and the correspondence with the CCC and/or CMC. The endpoints in the side-by-side tests **must** be based on the same amount of the same adverse effect so that the WER is a ratio of identical endpoints. The same computational method **must** be used for both tests used in the calculation of the WER.

c. Both total recoverable and dissolved results should be calculated for each test.

d. Results should be based on the time-weighted average measured metal concentrations (see Figure 6).

5. The acceptability of the laboratory dilution water **must** be evaluated by comparing results obtained with two sensitive tests using the laboratory dilution water with results that were obtained using a comparable laboratory dilution water in one or more other laboratories (see sections C.3.b and F.5).

a. If, after taking into account any known effect of hardness on toxicity, the new values for the endpoints of both of the tests are (1) more than a factor of 1.5 higher than the respective means of the values from the other laboratories or (2) more than a factor of 1.5 lower than the respective means of values from the other laboratories or (3) lower than the respective lowest values available from other laboratories or (4) higher than the respective highest values available from other laboratories, the new and old data **must** be carefully evaluated to determine whether the laboratory dilution water used in the WER determination was acceptable. For example, there might have been an error in the chemical measurements, which might mean that the results of all tests performed in the WER determination need to be adjusted and that the WER would not change. It is also possible that the metal is more or less toxic in the laboratory dilution water used in the WER determination. Further, if the new data were based on measured concentrations but the old data were based on nominal concentrations, the new data should probably be considered to be better than the old. Evaluation of results of any other toxicity tests on the same or a different metal using the same laboratory dilution water might be useful.

b. If, after taking into account any known effect of hardness on toxicity, the new values for the endpoints of the two tests are not either <u>both higher</u> or <u>both lower</u> in comparison than data from other laboratories (as per section a above) and if both of the new values are within a factor of 2 of the respective means of the previously available values or are within the ranges of the values, the laboratory dilution water used in the WER determination is acceptable.

c. A control chart approach may be used if sufficient data are available.

d. If the comparisons do not indicate that the laboratory dilution water, test method, etc., are acceptable, the tests probably should be considered unacceptable, unless other toxicity data are available to indicate that they are acceptable.

Comparison of results of tests between laboratories provides a check on all aspects of the test procedure; the emphasis here is on the quality of the laboratory dilution water because all other aspects of the side-by-side tests on which the WER is based **must** be the same, except possibly for the concentrations of metal used and the acclimation just prior to the beginning of the tests.

6. If all the necessary tests and the laboratory dilution water are acceptable, a WER **must** be calculated by dividing the endpoint obtained using site water by the endpoint obtained using laboratory dilution water.
   a. If both a primary test and a secondary test were conducted using both waters, WERs **must** be calculated for both tests.
   b. Both total recoverable and dissolved WERs **must** be calculated.
   c. If the detection limit of the analytical method used to measure the metal is above the endpoint in laboratory dilution water, the detection limit **must** be used as the endpoint, which will result in a lower WER than would be obtained if the actual concentration had been measured. If the detection limit of the analytical method used is above the endpoint in site water, a WER cannot be determined.

7. Investigation of the WER.
   a. The results of the chemical measurements of hardness, alkalinity, pH, TSS, TOC, total recoverable metal, dissolved metal, etc., on the effluent and the upstream water should be examined and compared with previously available values for the effluent and upstream water,

respectively, to determine whether the samples were representative and to get some indication of the variability in the composition, especially as it might affect the toxicity of the metal and the WER, and to see if the WER correlates with one or more of the measurements.

b. The WERs obtained with the primary and secondary tests should be compared to determine whether the WER obtained with the secondary test confirmed the WER obtained with the primary test. Equally sensitive tests are expected to give WERs that are similar (e.g., within a factor of 3), whereas a test that is less sensitive will probably give a smaller WER than a more sensitive test (see Appendix D). Thus a WER obtained with a primary test is considered confirmed if either or both of the following are true:
   1) the WERs obtained with the primary and secondary tests are within a factor of 3.
   2) the test, regardless of whether it is the primary or secondary test, that gives a higher endpoint in the laboratory dilution water also gives the larger WER.

   If the WER obtained with the secondary test does not confirm the WER obtained with the primary test, the results should be investigated. In addition, WERs probably should be determined using both tests the next time samples are obtained and it would be desirable to determine a WER using a third test. It is also important to evaluate what the results imply about the protectiveness of any proposed site-specific criterion.

c. If the WER is larger than 5, it should be investigated.
   1) If the endpoint obtained using the laboratory dilution water was lower than previously reported lowest value or was more than a factor of two lower than an existing Species Mean Acute Value in a criteria document, additional tests in the laboratory dilution water are probably desirable.
   2) If a total recoverable WER was larger than 5 but the dissolved WER was not, is the metal one whose WER is likely to be affected by TSS and/or TOC and was the concentration of TSS and/or TOC high? Was there a substantial difference between the total recoverable and dissolved concentrations of the metal in the downstream water?
   3) If both the total recoverable and dissolved WERs were larger than 5, is it likely that there is nontoxic dissolved metal in the downstream water?

d. The adverse effects and the time-course of effects in the side-by-side tests should be compared. If they are different, it might indicate that the site-water test is questionable or that additivity, synergism, or antagonism occurred in the site water. This might be especially important if the WER obtained with the secondary test did not confirm the WER obtained with the primary test or if the WER was very large or small.

8. If at least one WER determined with the primary test was confirmed by a WER that was simultaneously determined with the secondary test, the cmcFWER and/or the cccFWER should be derived as described in section A.5.

9. All data generated during the determination of the WER should be examined to see if there are any implications for the national or site-specific aquatic life criterion.
   a. If there are data for a species for which data were not previously available or unusual data for a species for which data were available, the national criterion might need to be revised.
   b. If the primary test gives an LC50 or EC50 in laboratory dilution water that is the same as the national CMC, the resulting site-specific CMC should be similar to the LC50 that was obtained with the primary test using downstream water. Such relationships might serve as a check on the applicability of the use of WERs.
   c. If data indicate that the site-specific criterion would not adequately protect a critical species, the site-specific criterion probably should be lowered.

J. Reporting the Results

A report of the experimental determination of a WER to the appropriate regulatory authority **must** include the following:
1. Name(s) of the investigator(s), name and location of the laboratory, and dates of initiation and termination of the tests.
2. A description of the laboratory dilution water, including source, preparation, and any demonstrations that an aquatic species can survive, grow, and reproduce in it.
3. The name, location, and description of the discharger, a description of the effluent, and the design flows of the effluent and the upstream water.
4. A description of each sampling station, date, and time, with an explanation of why they were selected, and the flows of the upstream water and the effluent at the time the samples were collected.
5. The procedures used to obtain, transport, and store the samples of the upstream water and the effluent.
6. Any pretreatment, such as filtration, of the effluent, site water, and/or laboratory dilution water.
7. Results of all chemical and physical measurements on upstream water, effluent, actual and/or simulated downstream water, and laboratory dilution water, including hardness (or salinity), alkalinity, pH, and concentrations of total recoverable metal, dissolved metal, TSS, and TOC.

8. Description of the experimental design, test chambers, depth and volume of solution in the chambers, loading and lighting, and numbers of organisms and chambers per treatment.
9. Source and grade of the metallic salt, and how the stock solution was prepared, including any acids or bases used.
10. Source of the test organisms, scientific name and how verified, age, life stage, means and ranges of weights and/or lengths, observed diseases, treatments, holding and acclimation procedures, and food.
11. The average and range of the temperature, pH, hardness (or salinity), and the concentration of dissolved oxygen (as % saturation and as mg/L) during acclimation, and the method used to measure them.
12. The following **must** be presented for each toxicity test:
    a. The average and range of the measured concentrations of dissolved oxygen, as % saturation and as mg/L.
    b. The average and range of the test temperature and the method used to measure it.
    c. The schedule for taking samples of test solutions and the methods used to obtain, prepare, and store them.
    d. A summary table of the total recoverable and dissolved concentrations of the metal in each treatment, including all controls, in which they were measured.
    e. A summary table of the values of the toxicological variable(s) for each treatment, including all controls, in sufficient detail to allow an independent statistical analysis of the data.
    f. The endpoint and the method used to calculate it.
    g. Comparisons with other data obtained by conducting the same test on the same metal using laboratory dilution water in the same and different laboratories; such data may be from a criteria document or from another source.
    h. Anything unusual about the test, any deviations from the procedures described above, and any other relevant information.
13. All differences, other than the dilution water and the concentrations of metal in the test solutions, between the side-by-side tests using laboratory dilution water and site water.
14. Comparison of results obtained with the primary and secondary tests.
15. The WER and an explanation of its calculation.

A report of the derivation of a FWER **must** include the following:

1. A report of the determination of each WER that was determined for the derivation of the FWER; all WERs determined with secondary tests **must** be reported along with all WERs that were determined with the primary test.

2. The design flow of the upstream water and the effluent and the hardness used in the derivation of the permit limits, if the criterion for the metal is hardness-dependent.
3. A summary table **must** be presented that contains the following for each WER that was derived:
   a. the value of the WER and the two endpoints from which it was calculated.
   b. the hWER calculated from the WER.
   c. the test and species that was used.
   d. the date the samples of effluent and site water were collected.
   e. the flows of the effluent and upstream water when the samples were taken.
   f. the following information concerning the laboratory dilution water, effluent, upstream water, and actual and/or simulated downstream water: hardness (salinity), alkalinity, pH, and concentrations of total recoverable metal, dissolved metal, TSS, and TOC.
4. A detailed explanation of how the FWER was derived from the WERs that are in the summary table.

METHOD 2: DETERMINING cccWERs FOR AREAS AWAY FROM PLUMES

Method 2 might be viewed as a simple process wherein samples of site water are obtained from locations within a large body of fresh or salt water (e.g., an ocean or a large lake, reservoir, or estuary), a WER is determined for each sample, and the FWER is calculated as the geometric mean of some or all of the WERs. In reality, Method 2 is not likely to produce useful results unless substantial resources are devoted to planning and conducting the study. Most sites to which Method 2 is applied will have long retention times, complex mixing patterns, and a number of dischargers. Because metals are persistent, the long retention times mean that the sites are likely to be defined to cover rather large areas; thus such sites will herein be referred to generically as "large sites". Despite the differences between them, all large sites require similar special considerations regarding the determination of WERs. Because Method 2 is based on samples of actual surface water (rather than simulated surface water), no sample should be taken in the vicinity of a plume and the method should be used to determine cccWERs, not cmcWERs. If WERs are to be determined for more than one metal, Appendix F should be read.

Method 2 uses many of the same methodologies as Method 1, such as those for toxicity tests and chemical analyses. Because the sampling plan is crucial to Method 2 and the plan has to be based on site-specific considerations, this description of Method 2 will be more qualitative than the description of Method 1.

Method 2 is based on use of actual surface water samples, but use of simulated surface water might provide information that is useful for some purposes:

1. It might be desirable to compare the WERs for two discharges that contain the same metal. This might be accomplished by selecting an appropriate dilution water and preparing two simulated surface waters, one that contains a known concentration of one effluent and one that contains a known concentration of the other effluent. The relative magnitude of the two WERs is likely to be more useful than the absolute values of the WERs themselves.
2. It might be desirable to determine whether the eWER for a particular effluent is additive with the WER of the site water (see Appendix G). This can be studied by determining WERs for several different known concentrations of the effluent in site water.
3. An event such as a rain might affect the WER because of a change in the water quality, but it might also reduce the WER just by dilution of refractory metal or TSS. A proportional decrease in the WER and in the concentration of the metal (such as by dilution of refractory metal) will not result in underprotection; if, however, dilution decreases the WER

proportionally more than it decreases the concentration of metal in the downstream water, underprotection is likely to occur. This is essentially a determination of whether the WER is additive when the effluent is diluted with rain water (see Appendix G).

4. An event that increases TSS might increase the total recoverable concentration of the metal and the total recoverable WER without having much effect on either the dissolved concentration or the dissolved WER.

In all four cases, the use of simulated surface water is useful because it allows for the determination of WERs using known concentrations of effluent.

An important step in the determination of any WER is to define the area to be included in the site. The major principle that should be applied when defining the area is the same for all sites: The site should be neither too small nor too large. If the area selected is too small, permit limits might be unnecessarily controlled by a criterion for an area outside the site, whereas too large an area might unnecessarily incorporate spatial complexities that are not relevant to the discharge(s) of concern and thereby unnecessarily increase the cost of determining the WER. Applying this principle is likely to be more difficult for large sites than for flowing-water sites.

Because WERs for large sites will usually be determined using actual, rather than simulated, surface water, there are five major considerations regarding experimental design and data analysis:

1. Total recoverable WERs at large sites might vary so much across time, location, and depth that they are not very useful. An assumption should be developed that an appropriately defined WER will be much more similar across time, location, and depth within the site than will a total recoverable WER. If such an assumption cannot be used, it is likely that either the FWER will have to be set equal to the lowest WER and be overprotective for most of the site or separate site-specific criteria will have to be derived for two or more sites.
   a. One assumption that is likely to be worth testing is that the dissolved WER varies much less across time, location, and depth within a site than the total recoverable WER. If the assumption proves valid, a dissolved WER can be applied to a dissolved national water quality criterion to derive a dissolved site-specific water quality criterion that will apply to the whole site.
   b. A second assumption that might be worth testing is that the WER correlates with a water quality characteristic such as TSS or TOC across time, location, and depth.
   c. Another assumption that might be worth testing is that the dissolved and/or total recoverable WER is mostly due to

nontoxic metal rather than to a water quality characteristic that reduces toxicity. If this is true and if there is variability in the WER, the WER will correlate with the concentration of metal in the site water. This is similar to the first assumption, but this one can allow use of both total recoverable and dissolved WERs, whereas the first one only allows use of a dissolved WER.

If WERs are too variable to be useful and no way can be found to deal with the variability, additional sampling will probably be required in order to develop a WER and/or a site-specific water quality criterion that is either (a) spatially and/or temporally dependent or (b) constant and environmentally conservative for nearly all conditions.

2. An experimental design should be developed that tests whether the assumption is of practical value across the range of conditions that occur at different times, locations, and depths within the site. Each design has to be formulated individually to fit the specific site. The design should try to take into account the times, locations, and depths at which the extremes of the physical, chemical, and biological conditions occur within the site, which will require detailed information concerning the site. In addition, the experimental design should balance available resources with the need for adequate sampling.
    a. Selection of the number and timing of sampling events should take into account seasonal, weekly, and daily considerations. Intensive sampling should occur during the two most extreme seasons, with confirmatory sampling during the other two seasons. Selection of the day and time of sample collection should take into account the discharge schedules of the major industrial and/or municipal discharges. For example, it might be appropriate to collect samples during the middle of the week to allow for reestablishment of steady-state conditions after shutdowns for weekends and holidays; alternatively, end-of-the-week slug discharges are routine in some situations. In coastal sites, the tidal cycle might be important if facilities discharge, for example, over a four-hour period beginning at slack high tide. Because the highest concentration of effluent in the surface water probably occurs at ebb tide, determination of WERs using site water samples obtained at this time might result in inappropriately large WERs that would result in underprotection at other times; samples with unusually large WERs might be especially useful for testing assumptions. The importance of each consideration should be determined on a case-by-case basis.
    b. Selection of the number and locations of stations to be sampled within a sampling event should consider the site as a whole and take into account sources of water and discharges, mixing patterns, and currents (and tides in coastal areas). If the site has been adequately

characterized, an acceptable design can probably be developed using existing information concerning (1) sources of the metal and other pollutants and (2) the spatial and temporal distribution of concentrations of the metal and water quality factors that might affect the toxicity of the metal. Samples should not be taken within or near mixing zones or plumes of dischargers; dilution models (U.S. EPA 1993) and dye dispersion studies (Kilpatrick 1992) can indicate areas that should definitely be avoided. Maps, current charts, hydrodynamic models, and water quality models used to allocate waste loads and derive permit limits are likely to be helpful when determining when and where to obtain site-water samples. Available information might provide an indication of the acceptability of site water for testing selected species. The larger and more complex the site, the greater the number of sampling locations that will be needed.

c. In addition to determining the horizontal location of each sampling station, the vertical location (i.e., depth) of the sampling point needs to be selected. Known mixing regimes, the presence of vertical stratification of TSS and/or salinity, concentration of metal, effluent plumes, tolerance of test species, and the need to obtain samples of site water that span the range of site conditions should be considered when selecting the depth at which the sample is to be taken. Some decisions concerning depth cannot be made until information is obtained at the time of sampling; for example, a conductivity meter, salinometer, or transmissometer might be useful for determining where and at what depth to collect samples. Turbidity might correlate with TSS and both might relate to the toxicity of the metal in site water; salinity can indicate whether the test organisms and the site water are compatible.

Because each site is unique, specific guidance cannot be given here concerning either the selection of the appropriate number and locations of sampling stations within a site or the frequency of sampling. All available information concerning the site should be utilized to ensure that the times, locations, and depths of samples span the range of water quality characteristics that might affect the toxicity of the metal:

a. High and low concentrations of TSS.
b. High and low concentrations of effluents.
c. Seasonal effects.
d. The range of tidal conditions in saltwater situations.

The sampling plan should provide the data needed to allow an evaluation of the usefulness of the assumption(s) that the experimental design is intended to test. Statisticians should play a key role in experimental design and data analysis, but professional judgment that takes into account pertinent biological, chemical, and toxicological considerations is at least as important as rigorous statistical analysis when interpreting the data and determining the degree to which the data correspond to the assumption(s).

3. The details of each sampling design should be formulated with the aid of people who understand the site and people who have a working knowledge of WERs. Because of the complexity of designing a WER study for large sites, the design team should utilize the combined expertise and experience of individuals from the appropriate EPA Region, states, municipalities, dischargers, environmental groups, and others who can constructively contribute to the design of the study. Building a team of cooperating aquatic toxicologists, aquatic chemists, limnologists, oceanographers, water quality modelers, statisticians, individuals from other key disciplines, as well as regulators and those regulated, who have knowledge of the site and the site-specific procedures, is central to success of the derivation of a WER for a large site. Rather than submitting the workplan to the appropriate regulatory authority (and possibly the Water Management Division of the EPA Regional Office) for comment at the end, they should be members of the team from the beginning.

4. Data from one sampling event should always be analyzed prior to the next sampling event with the goal of improving the sampling design as the study progresses. For example, if the toxicity of the metal in surface water samples is related to the concentration of TSS, a water quality characteristic such as turbidity might be measured at the time of collection of water samples and used in the selection of the concentrations to be used in the WER toxicity tests in site water. At a minimum, the team that interprets the results of one sampling event and plans the next should include an aquatic toxicologist, a metals chemist, a statistician, and a modeler or other user of the data.

5. The final interpretation of the data and the derivation of the FWER(s) should be performed by a team. Sufficient data are likely to be available to allow a quantitative estimate of experimental variation, differences between species, and seasonal differences. It will be necessary to decide whether one site-specific criterion can be applied to the whole area or whether separate site-specific criteria need to be derived for two or more sites. The interpretation of the data might produce two or more alternatives that the appropriate regulatory authority could subject to a cost-benefit analysis.

Other aspects of the determination of a WER for a large site are likely to be the same as described for Method 1. For example:

a. WERs should be determined using two or more sensitive species; the suggestions given in Appendix I should be considered when selecting the tests and species to be used.

b. Chemical analyses of site water, laboratory dilution water, and test solutions should follow the requirements for the specific test used and those given in this document.
c. If tests in many surface water samples are compared to one test in a laboratory dilution water, it is very important that that one test be acceptable. Use of (1) rangefinding tests, (2) additional treatments beyond the standard five concentrations plus controls, and (3) dilutions that are functions of the known concentration-effect relationships obtained with the toxicity test and metal of concern will help ensure that the desired endpoints and WERs can be calculated.
d. Measurements of the concentrations of both total recoverable and dissolved metal should be targeted to the test concentrations whose data will be used in the calculation of the endpoints.
e. Samples of site water and/or effluent should be collected, handled, and transported so that the tests can begin as soon as is feasible.
f. If the large site is a saltwater site, the considerations presented in Appendix H ought to be given attention.

Figure 2: Calculating an Adjusted Geometric Mean

Where n = the number of experimentally determined WERs in a set, the "adjusted geometric mean" of the set is calculated as follows:

a. Take the logarithm of each of the WERs. The logarithms can be to any base, but natural logarithms (base e) are preferred for reporting purposes.
b. Calculate $\overline{x}$ = the arithmetic mean of the logarithms.
c. Calculate s = the sample standard deviation of the logarithms:

$$s = \sqrt{\frac{(x - \overline{x})^2}{n - 1}} .$$

d. Calculate SE = the standard error of the arithmetic mean: $SE = s/\sqrt{n}$.
e. Calculate $A = \overline{x} - (t_{0.7})(SE)$, where $t_{0.7}$ is the value of Student's t statistic for a one-sided probability of 0.70 with $n - 1$ degrees of freedom. The values of $t_{0.7}$ for some common degrees of freedom (df) are:

df	$t_{0.7}$
1	0.727
2	0.617
3	0.584
4	0.569
5	0.559
6	0.553
7	0.549
8	0.546
9	0.543
10	0.542
11	0.540
12	0.539

The values of $t_{0.7}$ for more degrees of freedom are available, for example, on page T-5 of Natrella (1966).
f. Take the antilogarithm of A.

This adjustment of the geometric mean accounts for the fact that the means of fifty percent of the sets of WERs are expected to be higher than the actual mean; using the one-sided value of t for 0.70 reduces the percentage to thirty.

Figure 3: An Example Derivation of a FWER

This example assumes that cccWERs were determined monthly using simulated downstream water that was prepared by mixing upstream water with effluent at the ratio that existed when the samples were obtained. Also, the flow of the effluent is always 10 cfs, and the design flow of the upstream water is 40 cfs. (Therefore, the downstream flow at design-flow conditions is 50 cfs.) The concentration of metal in upstream water at design flow is 0.4 ug/L, and the CCC is 2 ug/L. Each FWER is derived from the WERs and hWERs that are available through that month.

Month	eFLOW (cfs)	uFLOW (cfs)	uCONC (ug/L)	WER	HCME (ug/L)	hWER	FWER
March	10	850	0.8	5.2[a]	826.4	82.80	1.0[b]
April	10	289	0.6	6.0[c]	341.5	34.31	1.0[b]
May	10	300	0.6	5.8[c]	341.6	34.32	1.0[b]
June	10	430	0.6	5.7[c]	475.8	47.74	5.7[d]
July	10	120	0.4	7.0[c]	177.2	17.88	5.7[d]
Aug.	10	85	0.4	10.5[e]	196.1	19.77	6.80[f]
Sept.	10	40	0.4	12.0[e]	118.4	12.00	10.69[g]
Oct.	10	45	0.4	11.0[e]	119.2	12.08	10.88[g]
Nov.	10	150	0.4	7.5[c]	234.0	23.56	10.88[g]
Dec.	10	110	0.4	3.5[c]	79.6	8.12	8.12[h]
Jan.	10	180	0.6	6.9[c]	251.4	25.30	8.12[h]
Feb.	10	244	0.6	6.1[c]	295.2	29.68	8.12[h]

a Neither Type 1 nor Type 2; the downstream flow (i.e., the sum of the eFLOW and the uFLOW) is > 500 cfs.

b The total number of available Type 1 and Type 2 WERs is less than 3.

c A Type 2 WER; the downstream flow is between 100 and 500 cfs.

d No Type 1 WER is available; the FWER is the lower of the lowest Type 2 WER and the lowest hWER.

e A Type 1 WER; the downstream flow is between 50 and 100 cfs.

f One Type 1 WER is available; the FWER is the geometric mean of all Type 1 and Type 2 WERs.

g Two or more Type 1 WERs are available and the range is less than a factor of 5; the FWER is the adjusted geometric mean (see Figure 2) of the Type 1 WERs, because all the hWERs are higher.

h Two or more Type 1 WERs are available and the range is not greater than a factor of 5; the FWER is the lowest hWER because the lowest hWER is lower than the adjusted geometric mean of the Type 1 WERs.

Figure 4: Reducing the Impact of Experimental Variation

When the FWER is the lowest of, for example, three WERs, the impact of experimental variation can be reduced by conducting additional primary tests. If the endpoint of the secondary test is above the CMC or CCC to which the FWER is to be applied, the additional tests can also be conducted with the secondary test.

Month	Case 1	Case 2		
	(Primary Test)	(Primary Test)	(Primary Test)	Geometric Mean
April	4.801	4.801	3.565	4.137
May	2.552	2.552	4.190	3.270
June	9.164	9.164	6.736	7.857
Lowest	2.552			3.270

Month	Case 3			Case 4		
	(Primary Test)	(Second. Test)	Geo. Mean	(Primary Test)	(Second. Test)	Geo. Mean
April	4.801	3.163	3.897	4.801	3.163	3.897
May	2.552	5.039	3.586	2.552	2.944	2.741
June	9.164	7.110	8.072	9.164	7.110	8.072
Lowest			3.586			2.741

Case 1 uses the individual WERs obtained with the primary test for the three months, and the FWER is the lowest of the three WERs. In Case 2, duplicate primary tests were conducted in each month, so that a geometric mean could be calculated for each month; the FWER is the lowest of the three geometric means.

In Cases 3 and 4, both a primary test and a secondary test were conducted each month and the endpoints for both tests in laboratory dilution water are above the CMC or CCC to which the FWER is to be applied. In both of these cases, therefore, the FWER is the lowest of the three geometric means.

The availability of these alternatives does not mean that they are necessarily cost-effective.

Figure 5: Calculating an LC50 (or EC50) by Interpolation

When fewer than two treatments kill some but not all of the exposed test organisms, a statistically sound estimate of an LC50 cannot be calculated. Some programs and methods produce LC50s when there are fewer than two "partial kills", but such results are obtained using interpolation, not statistics. If (a) a test is otherwise acceptable, (b) a sufficient number of organisms are exposed to each treatment, and (c) the concentrations are sufficiently close together, a test with zero or one partial kill can provide all the information that is needed concerning the LC50. An LC50 calculated by interpolation should probably be called an "approximate LC50" to acknowledge the lack of a statistical basis for its calculation, but this does not imply that such an LC50 provides no useful toxicological information. If desired, the binomial test can be used to calculate a statistically sound probability that the true LC50 lies between two tested concentrations (Stephan 1977).

Although more complex interpolation methods can be used, they will not produce a more useful LC50 than the method described here. Inversions in the data between two test concentrations should be removed by pooling the mortality data for those two concentrations and calculating a percent mortality that is then assigned to both concentrations. Logarithms to a base other than 10 can be used if desired. If P1 and P2 are the percentages of the test organisms that died when exposed to concentrations C1 and C2, respectively, and if $C1 < C2$, $P1 < P2$, $0 \le P1 \le 50$, and $50 \le P2 \le 100$, then:

$$P = \frac{50 - P1}{P2 - P1}$$

$$C = Log\ C1 + P(Log\ C2 - Log\ C1)$$

$$LC50 = 10^{C}$$

If P1 = 0 and P2 = 100, $LC50 = \sqrt{(C1)(C2)}$.
If P1 = P2 = 50, $LC50 = \sqrt{(C1)(C2)}$.
If P1 = 50, LC50 = C1.
If P2 = 50, LC50 = C2.
If C1 = 4 mg/L, C2 = 7 mg/L, P1 = 15 %, and P2 = 100 %, then LC50 = 5.036565 mg/L.

Besides the mathematical requirements given above, the following toxicological recommendations are given in sections G.8 and I.2:
a. $0.65 < C1/C2 < 0.99$.
b. $0 \le P1 < 37$.
c. $63 < P2 \le 100$.

Figure 6: Calculating a Time-Weighted Average

If a sampling plan (e.g., for measuring metal in a treatment in a toxicity test) is designed so that a series of values are obtained over time in such a way that each value contains the same amount of information (i.e., represents the same amount of time), then the most meaningful average is the arithmetic average. In most cases, however, when a series of values is obtained over time, some values contain more information than others; in these cases the most meaningful average is a time-weighted average (TWA). If each value contains the same amount of information, the arithmetic average will equal the TWA.

A TWA is obtained by multiplying each value by a weight and then dividing the sum of the products by the sum of the weights. The simplest approach is to let each weight be the duration of time that the sample represents. Except for the first and last samples, the period of time represented by a sample starts halfway to the previous sample and ends halfway to the next sample. The period of time represented by the first sample starts at the beginning of the test, and the period of time represented by the last sample ends at the end of the test. Thus for a 96-hr toxicity test, the sum of the weights will be 96 hr.

The following are hypothetical examples of grab samples taken from 96-hr flow-through tests for two common sampling regimes:

Sampling time (hr)	Conc. (mg/L)	Weight (hr)	Product (hr) (mg/L)	Time-weighted average (mg/L)
0	12	48	576	
96	14	48	672	
		96	1248	1248/96 = 13.00
0	8	12	96	
24	6	24	144	
48	7	24	168	
72	9	24	216	
96	8	12	96	
		96	720	720/96 = 7.500

When all the weights are the same, the arithmetic average equals the TWA. Similarly, if only one sample is taken, both the arithmetic average and the TWA equal the value of that sample.

The rules are more complex for composite samples and for samples from renewal tests. In all cases, however, the sampling plan can be designed so that the TWA equals the arithmetic average.

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Appendix A: Comparison of WERs Determined Using Upstream and Downstream Water

The "Interim Guidance" concerning metals (U.S. EPA 1992) made a fundamental change in the way WERs should be experimentally determined because it changed the source of the site water. The earlier guidance (U.S. EPA 1983,1984) required that upstream water be used as the site water, whereas the newer guidance (U.S. EPA 1992) recommended that downstream water be used as the site water. The change in the source of the site water was merely an acknowledgement that the WER that applies at a location in a body of water should, when possible, be determined using the water that occurs at that location.

Because the change in the source of the dilution water was expected to result in an increase in the magnitude of many WERs, interest in and concern about the determination and use of WERs increased. When upstream water was the required site water, it was expected that WERs would generally be low and that the determination and use of WERs could be fairly simple. After downstream water became the recommended site water, the determination and use of WERs was examined much more closely. It was then realized that the determination and use of upstream WERs was more complex than originally thought. It was also realized that the use of downstream water greatly increased the complexity and was likely to increase both the magnitude and the variability of many WERs. Concern about the fate of discharged metal also increased because use of downstream water might allow the discharge of large amounts of metal that has reduced or no toxicity at the end of the pipe. The probable increases in the complexity, magnitude, and variability of WERs and the increased concern about fate, increased the importance of understanding the relevant issues as they apply to WERs determined using both upstream water and downstream water.

A. Characteristics of the Site Water

The idealized concept of an upstream water is a pristine water that is relatively unaffected by people. In the real world, however, many upstream waters contain naturally occurring ligands, one or more effluents, and materials from nonpoint sources; all of these might impact a WER. If the upstream water receives an effluent containing TOC and/or TSS that contributes to the WER, the WER will probably change whenever the quality or quantity of the TOC and/or TSS changes. In such a case, the determination and use of the WER in upstream water will have some of the increased complexity associated with use of downstream water and some of the concerns associated with multiple-discharge situations (see Appendix F). The amount of complexity will depend greatly on the number and type of upstream point and nonpoint sources, the frequency and magnitude of fluctuations, and whether the WER is being determined above or below the point of complete mix of the upstream sources.

Downstream water is a mixture of effluent and upstream water, each of which can contribute to the WER, and so there are two components to a WER determined in downstream water: the effluent component and the upstream component. The existence of these two components has the following implications:

1. WERs determined using downstream water are likely to be larger and more variable than WERs determined using upstream water.
2. The effluent component should be applied only where the effluent occurs, which has implications concerning implementation.
3. The magnitude of the effluent component of a WER will depend on the concentration of effluent in the downstream water. (A consequence of this is that the effluent component will be zero where the concentration of effluent is zero, which is the point of item 2 above.)
4. The magnitude of the effluent component of a WER is likely to vary as the composition of the effluent varies.
5. Compared to upstream water, many effluents contain higher concentrations of a wider variety of substances that can impact the toxicity of metals in a wider variety of ways, and so the effluent component of a WER can be due to a variety of chemical effects in addition to such factors as hardness, alkalinity, pH, and humic acid.
6. Because the effluent component might be due, in whole or in part, to the discharge of refractory metal (see Appendix D), the WER cannot be thought of simply as being caused by the effect of water quality on the toxicity of the metal.

Dealing with downstream WERs is so much simpler if the effluent WER (eWER) and the upstream WER (uWER) are additive that it is desirable to understand the concept of additivity of WERs, its experimental determination, and its use (see Appendix G).

B. The Implications of Mixing Zones.

When WERs are determined using upstream water, the presence or absence of mixing zones has no impact; the cmcWER and the cccWER will both be determined using site water that contains zero percent of the effluent of concern, i.e., the two WERs will be determined using the same site water.

When WERs are determined using downstream water, the magnitude of each WER will probably depend on the concentration of effluent in the downstream water used (see Appendix D). The concentration of effluent in the site water will depend on where the sample is taken, which will not be the same for the cmcWER and the cccWER if there are mixing zone(s). Most, if not all, discharges have a chronic (CCC) mixing zone; many, but not all, also have an acute (CMC) mixing zone. The CMC applies at all points except those inside a CMC mixing zone; thus if there is no CMC mixing zone, the CMC applies at the end of the pipe. The CCC applies at all points outside the CCC mixing zone. It is generally assumed that if permit limits are based on a point in a stream at which both the CMC and the CCC apply, the CCC will control the permit limits, although the CMC might control if different averaging periods are appropriately taken into account. For this discussion, it will be assumed that the same design flow (e.g., 7Q10) is used for both the CMC and the CCC.

If the cmcWER is to be appropriate for use inside the chronic mixing zone, but the cccWER is to be appropriate for use outside the chronic mixing zone, the concentration of effluent that is appropriate for use in the determination of the two WERs will not be the same. Thus even if the same toxicity test is used in the determination of the cmcWER and the cccWER, the two WERs will probably be different because the concentration of effluent will be different in the two site waters in which the WERs are determined.

If the CMC is only of concern within the CCC mixing zone, the highest relevant concentration of metal will occur at the edge of the CMC mixing zone if there is a CMC mixing zone; the highest concentration will occur at the end of the pipe if there is no CMC mixing zone. In contrast, within the CCC mixing zone, the lowest cmcWER will probably occur at the outer edge of the CCC mixing zone. Thus the greatest level of protection would be provided if the cmcWER is determined using water at the outer edge of the CCC mixing zone, and then the calculated site-specific CMC is applied at the edge of the CMC mixing zone or at the end of the pipe, depending on whether there is an acute mixing zone. The cmcWER is likely to be lowest at the outer edge of the CCC mixing zone because of dilution of the effluent, but this dilution will also dilute the metal. If the cmcWER is determined at the outer edge of the CCC mixing zone but the resulting site-specific CMC is applied at the end of the pipe or at the edge of the CMC mixing zone, dilution is allowed to reduce the WER but it is not allowed to reduce the concentration of the metal. This approach is environmentally conservative, but it is probably necessary given current implementation procedures. (The situation might be more complicated if the uWER is higher than the eWER or if the two WERs are less-than-additive.)

A comparable situation applies to the CCC. Outside the CCC mixing zone, the CMC and the CCC both apply, but it is assumed that the CMC can be ignored because the CCC will be more restrictive. The cccWER should probably be determined for the complete-mix situation, but the site-specific CCC will have to be met at the edge of the CCC mixing zone. Thus dilution of the WER from the edge of the CCC mixing zone to the point of complete mix is taken into account, but dilution of the metal is not.

If there is neither an acute nor a chronic mixing zone, both the CMC and the CCC apply at the end of the pipe, but the CCC should still be determined for the complete-mix situation.

C. Definition of site.

In the general context of site-specific criteria, a "site" may be a state, region, watershed, waterbody, segment of a waterbody, category of water (e.g., ephemeral streams), etc., but the site-specific criterion is to be derived to provide adequate protection for the entire site, however the site is defined. Thus, when a site-specific criterion is derived using the Recalculation Procedure, all species that "occur at the site" need to be taken into account when deciding what species, if any, are to be deleted from the dataset. Similarly, when a site-specific criterion is derived using a WER, the WER is to be adequately protective of the entire site. If, for example, a site-specific criterion is being derived for an estuary, WERs could be determined using samples of the surface water obtained from various sampling stations, which, to avoid confusion, should not be called "sites". If all the WERs were sufficiently similar, one site-specific criterion could be derived to apply to the whole estuary. If the WERs were sufficiently different, either the lowest WER could be used to derive a site-specific criterion for the whole estuary, or the data might indicate that the estuary should be divided into two or more sites, each with its own criterion.

The major principle that should be applied when defining the area to be included in the site is very simplistic: The site should be neither too small nor too large.

1. Small sites are probably appropriate for cmcWERs, but usually are not appropriate for cccWERs because metals are persistent, although some oxidation states are not persistent and some metals are not persistent in the water column. For cccWERs, the smaller the defined site, the more likely it is that the permit limits will be controlled by a criterion for an area that is outside the site, but which could have been included in the site without substantially changing the WER or increasing the cost of determining the WER.
2. Too large an area might unnecessarily increase the cost of determining the WER. As the size of the site increases,

the spatial and temporal variability is likely to increase, which will probably increase the number of water samples in which WERs will need to be determined before a site-specific criterion can be derived.

3. Events that import or resuspend TSS and/or TOC are likely to increase the total recoverable concentration of the metal and the total recoverable WER while having a much smaller effect on the dissolved concentration and the dissolved WER. Where the concentration of dissolved metal is substantially more constant than the concentration of total recoverable metal, the site can probably be much larger for a dissolved criterion than for a total recoverable criterion. If one criterion is not feasible for the whole area, it might be possible to divide it into two or more sites with separate total recoverable or dissolved criteria or to make the criterion dependent on a water quality characteristic such as TSS or salinity.
4. Unless the site ends where one body of water meets another, at the outer edge of the site there will usually be an instantaneous decrease in the allowed concentration of the metal in the water column due to the change from one criterion to another, but there will not be an instantaneous decrease in the actual concentration of metal in the water column. The site has to be large enough to include the transition zone in which the actual concentration decreases so that the criterion outside the site is not exceeded.

It is, of course, possible in some situations that relevant distant conditions (e.g., a lower downstream pH) will necessitate a low criterion that will control the permit limits such that it is pointless to determine a WER.

When a WER is determined in upstream water, it is generally assumed that a downstream effluent will not decrease the WER. It is therefore assumed that the site can usually cover a rather large geographic area.

When a site-specific criterion is derived based on WERs determined using downstream water, the site should not be defined in the same way that it would be defined if the WER were determined using upstream water. The eWER should be allowed to affect the site-specific criterion wherever the effluent occurs, but it should not be allowed to affect the criterion in places where the effluent does not occur. In addition, insofar as the magnitude of the effluent component at a point in the site depends on the concentration of effluent, the magnitude of the WER at a particular point will depend on the concentration of effluent at that point. To the extent that the eWER and the uWER are additive, the WER and the concentration of metal in the plume will decrease proportionally (see Appendix G).

When WERs are determined using downstream water, the following considerations should be taken into account when the site is defined:

1. If a site-specific criterion is derived using a WER that applies to the complete-mix situation, the upstream edge of the site to which this criterion applies should be the point at which complete mix actually occurs. If the site to which the complete-mix WER is applied starts at the end of the pipe and extends all the way across the stream, there will be an area beside the plume that will not be adequately protected by the site-specific criterion.
2. Upstream of the point of complete mix, it will usually be protective to apply a site-specific criterion that was derived using a WER that was determined using upstream water.
3. The plume might be an area in which the concentration of metal could exceed a site-specific criterion without causing toxicity because of simultaneous dilution of the metal and the eWER. The fact that the plume is much larger than the mixing zone might not be important if there is no toxicity within the plume. As long as the concentration of metal in 100 % effluent does not exceed that allowed by the additive portion of the eWER, from a toxicological standpoint neither the size nor the definition of the plume needs to be of concern because the metal will not cause toxicity within the plume. If there is no toxicity within the plume, the area in the plume might be like a traditional mixing zone in that the concentration of metal exceeds the site-specific criterion, but it would be different from a traditional mixing zone in that the level of protection is not reduced.

Special considerations are likely to be necessary in order to take into account the eWER when defining a site related to multiple discharges (see Appendix F).

D. The variability in the experimental determination of a WER.

When a WER is determined using upstream water, the two major sources of variation in the WER are (a) variability in the quality of the site water, which might be related to season and/or flow, and (b) experimental variation. Ordinary day-to-day variation will account for some of the variability, but seasonal variation is likely to be more important.

As explained in Appendix D, variability in the concentration of nontoxic dissolved metal will contribute to the variability of both total recoverable WERs and dissolved WERs; variability in the concentration of nontoxic particulate metal will contribute to the variability in a total recoverable WER, but not to the variability in a dissolved WER. Thus, dissolved

WERs are expected to be less variable than total recoverable WERs, especially where events commonly increase TSS and/or TOC. In some cases, therefore, appropriate use of analytical chemistry can greatly increase the usefulness of the experimental determination of WERs. The concerns regarding variability are increased if an upstream effluent contributes to the WER.

When a WER is determined in downstream water, the four major sources of variability in the WER are (a) variability in the quality of the upstream water, which might be related to season and/or flow, (b) experimental variation, (c) variability in the composition of the effluent, and (d) variability in the ratio of the flows of the upstream water and the effluent. The considerations regarding the first two are the same as for WERs determined using upstream water; because of the additional sources of variability, WERs determined using downstream water are likely to be more variable than WERs determined using upstream water.

It would be desirable if a sufficient number of WERs could be determined to define the variable factors in the effluent and in the upstream water that contribute to the variability in WERs that are determined using downstream water. Not only is this likely to be very difficult in most cases, but it is also possible that the WER will be dependent on interactions between constituents of the effluent and the upstream water, i.e., the eWER and uWER might be additive, more-than-additive, or less-than-additive (see Appendix G). When interaction occurs, in order to completely understand the variability of WERs determined using downstream water, sufficient tests would have to be conducted to determine the means and variances of:

a. the effluent component of the WER.
b. the upstream component of the WER.
c. any interaction between the two components.

An interaction might occur, for example, if the toxicity of a metal is affected by pH, and the pH and/or the buffering capacity of the effluent and/or the upstream water vary considerably.

An increase in the variability of WERs decreases the usefulness of any one WER. Compensation for this decrease in usefulness can be attempted by determining WERs at more times; although this will provide more data, it will not necessarily provide a proportionate increase in understanding. Rather than determining WERs at more times, a better use of resources might be to obtain more information concerning a smaller number of specially selected occasions.

It is likely that some cases will be so complex that achieving even a reasonable understanding will require unreasonable resources. In contrast, some WERs determined using the methods presented herein might be relatively easy to understand if appropriate chemical measurements are performed when WERs are determined.

1. If the variation of the total recoverable WER is substantially greater than the variation of the comparable dissolved WER, there is probably a variable and substantial concentration of particulate nontoxic metal. It might be advantageous to use a dissolved WER just because it will have less variability than a total recoverable WER.
2. If the total recoverable and/or dissolved WER correlates with the total recoverable and/or dissolved concentration of metal in the site water, it is likely that a substantial percentage of the metal is nontoxic. In this case the WER will probably also depend on the concentration of effluent in the site water and on the concentration of metal in the effluent.

These approaches are more likely to be useful when WERs are determined using downstream water, rather than upstream water, unless both the magnitude of the WER and the concentration of the metal in the upstream water are elevated by an upstream effluent and/or events that increase TSS and/or TOC.

Both of these approaches can be applied to WERs that are determined using actual downstream water, but the second can probably provide much better information if it is used with WERs determined using simulated downstream water that is prepared by mixing a sample of the effluent with a sample of the upstream water. In this way the composition and characteristics of both the effluent and the upstream water can be determined, and the exact ratio in the downstream water is known.

Use of simulated downstream water is also a way to study the relation between the WER and the ratio of effluent to upstream water at one point in time, which is the most direct way to test for additivity of the eWER and the uWER (see Appendix G). This can be viewed as a test of the assumption that WERs determined using downstream water will decrease as the concentration of effluent decreases. If this assumption is true, as the flow increases, the concentration of effluent in the downstream water will decrease and the WER will decrease. Obtaining such information at one point in time is useful, but confirmation at one or more other times would be much more useful.

E. The fate of metal that has reduced or no toxicity.

Metal that has reduced or no toxicity at the end of the pipe might be more toxic at some time in the future. For example, metal that is in the water column and is not toxic now might become more toxic in the water column later or might move into the sediment and become toxic. If a WER allows a surface water to contain as much toxic metal as is acceptable, the WER would not be adequately protective if metal that was nontoxic when the WER was determined became toxic in the water column, unless a compensating change occurred. Studies of the fate of metals need to address not only the changes that take place, but also the rates of the changes.

Concern about the fate of discharged metal justifiably raises concern about the possibility that metals might contaminate sediments. The possibility of contamination of sediment by toxic and/or nontoxic metal in the water column was one of the concerns that led to the establishment of EPA's sediment quality criteria program, which is developing guidelines and criteria to protect sediment. A separate program was necessary because ambient water quality criteria are not designed to protect sediment. Insofar as technology-based controls and water quality criteria reduce the discharge of metals, they tend to reduce the possibility of contamination of sediment. Conversely, insofar as WERs allow an increase in the discharge of metals, they tend to increase the possibility of contamination of sediment.

When WERs are determined in upstream water, the concern about the fate of metal with reduced or no toxicity is usually small because the WERs are usually small. In addition, the factors that result in upstream WERs being greater than 1.0 usually are (a) natural organic materials such as humic acids and (b) water quality characteristics such as hardness, alkalinity, and pH. It is easy to assume that natural organic materials will not degrade rapidly, and it is easy to monitor changes in hardness, alkalinity, and pH. Thus there is usually little concern about the fate of the metal when WERs are determined in upstream water, especially if the WER is small. If the WER is large and possibly due at least in part to an upstream effluent, there is more concern about the fate of metal that has reduced or no toxicity.

When WERs are determined in downstream water, effluents are allowed to contain virtually unlimited amounts of nontoxic particulate metal and nontoxic dissolved metal. It would seem prudent to obtain some data concerning whether the nontoxic metal might become toxic at some time in the future whenever (1) the concentration of nontoxic metal is large, (2) the concentration of dissolved metal is below the dissolved national criterion but the concentration of total recoverable metal is substantially above the total recoverable national criterion, or (3) the site-specific criterion is substantially above the national criterion. It would seem appropriate to:

a. Generate some data concerning whether "fate" (i.e., environmental processes) will cause any of the nontoxic metal to become toxic due to oxidation of organic matter, oxidation of sulfides, etc. For example, a WER could be determined using a sample of actual or simulated downstream water, the sample aerated for a period of time (e.g., two weeks), the pH adjusted if necessary, and another WER determined. If aeration reduced the WER, shorter and longer periods of aeration could be used to study the rate of change.

b. Determine the effect of a change in water quality characteristics on the WER; for example, determine the effect of lowering the pH on the WER if influent lowers the pH of the downstream water within the area to which the site-specific criterion is to apply.
c. Determine a WER in actual downstream water to demonstrate whether downstream conditions change sufficiently (possibly due to degradation of organic matter, multiple dischargers, etc.) to lower the WER more than the concentration of the metal is lowered.

If environmental processes cause nontoxic metal to become toxic, it is important to determine whether the time scale involves days, weeks, or years.

<u>Summary</u>

When WERs are determined using downstream water, the site water contains effluent and the WER will take into account not only the constituents of the upstream water, but also the toxic and nontoxic metal and other constituents of the effluent as they exist after mixing with upstream water. The determination of the WER automatically takes into account any additivity, synergism, or antagonism between the metal and components of the effluent and/or the upstream water. The effect of calcium, magnesium, and various heavy metals on competitive binding by such organic materials as humic acid is also taken into account. Therefore, a site-specific criterion derived using a WER is likely to be more appropriate for a site than a national, state, or recalculated criterion not only because it takes into account the water quality characteristics of the site water but also because it takes into account other constituents in the effluent and upstream water.

Determination of WERs using downstream water causes a general increase in the complexity, magnitude, and variability of WERs, and an increase in concern about the fate of metal that has reduced or no toxicity at the end of the pipe. In addition, there are some other drawbacks with the use of downstream water in the determination of a WER:

1. It might serve as a disincentive for some dischargers to remove any more organic carbon and/or particulate matter than required, although WERs for some metals will not be related to the concentration of TOC or TSS.

2. If conditions change, a WER might decrease in the future. This is not a problem if the decrease is due to a reduction in nontoxic metal, but it might be a problem if the decrease is due to a decrease in TOC or TSS or an increase in competitive binding.
3. If a WER is determined when the effluent contains refractory metal but a change in operations results in the discharge of toxic metal in place of refractory metal, the site-specific criterion and the permit limits will not provide adequate protection. In most cases chemical monitoring probably will not detect such a change, but toxicological monitoring probably will.

Use of WERs that are determined using downstream water rather than upstream water increases:
1. The importance of understanding the various issues involved in the determination and use of WERs.
2. The importance of obtaining data that will provide understanding rather than obtaining data that will result in the highest or lowest WER.
3. The appropriateness of site-specific criteria.
4. The resources needed to determine a WER.
5. The resources needed to use a WER.
6. The resources needed to monitor the acceptability of the downstream water.

A WER determined using upstream water will usually be smaller, less variable, and simpler to implement than a WER determined using downstream water. Although in some situations a downstream WER might be smaller than an upstream WER, the important consideration is that a WER should be determined using the water to which it is to apply.

References

U.S. EPA. 1983. Water Quality Standards Handbook. Office of Water Regulations and Standards, Washington, DC.

U.S. EPA. 1984. Guidelines for Deriving Numerical Aquatic Site-Specific Water Quality Criteria by Modifying National Criteria. EPA-600/3-84-099 or PB85-121101. National Technical Information Service, Springfield, VA.

U.S. EPA. 1992. Interim Guidance on Interpretation and Implementation of Aquatic Life Criteria for Metals. Office of Science and Technology, Health and Ecological Criteria Division, Washington, DC.

Appendix B: The Recalculation Procedure

NOTE: The National Toxics Rule (NTR) does not allow use of the Recalculation Procedure in the derivation of a site-specific criterion. Thus nothing in this appendix applies to jurisdictions that are subject to the NTR.

The Recalculation Procedure is intended to cause a site-specific criterion to appropriately differ from a national aquatic life criterion if justified by demonstrated pertinent toxicological differences between the aquatic species that occur at the site and those that were used in the derivation of the national criterion. There are at least three reasons why such differences might exist between the two sets of species. First, the national dataset contains aquatic species that are sensitive to many pollutants, but these and comparably sensitive species might not occur at the site. Second, a species that is critical at the site might be sensitive to the pollutant and require a lower criterion. (A critical species is a species that is commercially or recreationally important at the site, a species that exists at the site and is listed as threatened or endangered under section 4 of the Endangered Species Act, or a species for which there is evidence that the loss of the species from the site is likely to cause an unacceptable impact on a commercially or recreationally important species, a threatened or endangered species, the abundances of a variety of other species, or the structure or function of the community.) Third, the species that occur at the site might represent a narrower mix of species than those in the national dataset due to a limited range of natural environmental conditions. The procedure presented here is structured so that corrections and additions can be made to the national dataset without the deletion process being used to take into account taxa that do and do not occur at the site; in effect, this procedure makes it possible to update the national aquatic life criterion.

The phrase "occur at the site" includes the species, genera, families, orders, classes, and phyla that:

a. are usually present at the site.
b. are present at the site only seasonally due to migration.
c. are present intermittently because they periodically return to or extend their ranges into the site.
d. were present at the site in the past, are not currently present at the site due to degraded conditions, and are expected to return to the site when conditions improve.
e. are present in nearby bodies of water, are not currently present at the site due to degraded conditions, and are expected to be present at the site when conditions improve.

The taxa that "occur at the site" cannot be determined merely by sampling downstream and/or upstream of the site at one point in time. "Occur at the site" does not include taxa that were once present at the site but cannot exist at the site now due to permanent physical alteration of the habitat at the site resulting from dams, etc.

The definition of the "site" can be extremely important when using the Recalculation Procedure. For example, the number of taxa that occur at the site will generally decrease as the size of the site decreases. Also, if the site is defined to be very small, the permit limit might be controlled by a criterion that applies outside (e.g., downstream of) the site.

Note: If the variety of aquatic invertebrates, amphibians, and fishes is so limited that species in <u>fewer than eight families</u> occur at the site, the general Recalculation Procedure is not applicable and the following special version of the Recalculation Procedure **must** be used:

1. Data **must** be available for at least one species in each of the families that occur at the site.
2. The lowest Species Mean Acute Value that is available for a species that occurs at the site **must** be used as the FAV.
3. The site-specific CMC and CCC **must** be calculated as described below in part 2 of step E, which is titled "Determination of the CMC and/or CCC".

The concept of the Recalculation Procedure is to create a dataset that is appropriate for deriving a site-specific criterion by modifying the national dataset in some or all of three ways:

a. Correction of data that are in the national dataset.
b. Addition of data to the national dataset.
c. Deletion of data that are in the national dataset.

All corrections and additions that have been approved by U.S. EPA are required, whereas use of the deletion process is optional. The Recalculation Procedure is more likely to result in lowering a criterion if the net result of addition and deletion is to decrease the number of genera in the dataset, whereas the procedure is more likely to result in raising a criterion if the net result of addition and deletion is to increase the number of genera in the dataset.

The Recalculation Procedure consists of the following steps:

A. Corrections are made in the national dataset.
B. Additions are made to the national dataset.
C. The deletion process may be applied if desired.
D. If the new dataset does not satisfy the applicable Minimum Data Requirements (MDRs), additional pertinent data **must** be generated; if the new data are approved by the U.S. EPA, the Recalculation Procedure **must** be started again at step B with the addition of the new data.
E. The new CMC or CCC or both are determined.
F. A report is written.

Each step is discussed in more detail below.

A. Corrections

1. Only corrections approved by the U.S. EPA may be made.
2. The concept of "correction" includes removal of data that should not have been in the national dataset in the first place. The concept of "correction" does not include removal of a datum from the national dataset just because the quality of the datum is claimed to be suspect. If additional data are available for the same species, the U.S. EPA will decide which data should be used, based on the available guidance (U.S. EPA 1985); also, data based on measured concentrations are usually preferable to those based on nominal concentrations.
3. Two kinds of corrections are possible:
   a. The first includes those corrections that are known to and have been approved by the U.S. EPA; a list of these will be available from the U.S. EPA.
   b. The second includes those corrections that are submitted to the U.S. EPA for approval. If approved, these will be added to EPA's list of approved corrections.
4. Selective corrections are not allowed. All corrections on EPA's newest list **must** be made.

B. Additions

1. Only additions approved by the U.S. EPA may be made.
2. Two kinds of additions are possible:
   a. The first includes those additions that are known to and have been approved by the U.S. EPA; a list of these will be available from the U.S. EPA.
   b. The second includes those additions that are submitted to the U.S. EPA for approval. If approved, these will be added to EPA's list of approved additions.
3. Selective additions are not allowed. All additions on EPA's newest list **must** be made.

C. The Deletion Process

The basic principles are:
1. Additions and corrections **must** be made as per steps A and B above, before the deletion process is performed.
2. Selective deletions are not allowed. If any species is to be deleted, the deletion process described below **must** be applied to all species in the national dataset, after any necessary corrections and additions have been made to the national dataset. The deletion process specifies which species **must** be deleted and which species **must not** be deleted. Use of the deletion process is optional, but no deletions are optional when the deletion process is used.
3. Comprehensive information **must** be available concerning what species occur at the site; a species cannot be deleted based

on incomplete information concerning the species that do and do not satisfy the definition of "occur at the site".

4. Data might have to be generated before the deletion process is begun:
   a. Acceptable pertinent toxicological data **must** be available for at least one species in each class of aquatic plants, invertebrates, amphibians, and fish that contains a species that is a critical species at the site.
   b. For each aquatic plant, invertebrate, amphibian, and fish species that occurs at the site and is listed as threatened or endangered under section 4 of the Endangered Species Act, data **must** be available or be generated for an acceptable surrogate species. Data for each surrogate species **must** be used as if they are data for species that occur at the site.

   If additional data are generated using acceptable procedures (U.S. EPA 1985) and they are approved by the U.S. EPA, the Recalculation Procedure **must** be started again at step B with the addition of the new data.
5. Data might have to be generated after the deletion process is completed. Even if one or more species are deleted, there still are MDRs (see step D below) that **must** be satisfied. If the data remaining after deletion do not satisfy the applicable MDRs, additional toxicity tests **must** be conducted using acceptable procedures (U.S. EPA 1985) so that all MDRs are satisfied. If the new data are approved by the U.S. EPA, the Recalculation Procedure **must** be started again at step B with the addition of new data.
6. Chronic tests do not have to be conducted because the national Final Acute-Chronic Ratio (FACR) may be used in the derivation of the site-specific Final Chronic Value (FCV). If acute-chronic ratios (ACRs) are available or are generated so that the chronic MDRs are satisfied using only species that occur at the site, a site-specific FACR may be derived and used in place of the national FACR. Because a FACR was not used in the derivation of the freshwater CCC for cadmium, this CCC can only be modified the same way as a FAV; what is acceptable will depend on which species are deleted.

If any species are to be deleted, the following deletion process **must** be applied:

a. Obtain a copy of the national dataset, i.e., tables 1, 2, and 3 in the national criteria document (see Appendix E).
b. Make corrections in and/or additions to the national dataset as described in steps A and B above.
c. Group all the species in the dataset taxonomically by phylum, class, order, family, genus, and species.
d. Circle each species that satisfies the definition of "occur at the site" as presented on the first page of this appendix, and including any data for species that are surrogates of threatened or endangered species that occur at the site.

e. Use the following step-wise process to determine which of the uncircled species **must** be deleted and which **must not** be deleted:

1. Does the genus occur at the site?
   - If "No", go to step 2.
   - If "Yes", are there one or more species in the genus that occur at the site but are not in the dataset?
     - If "No", go to step 2.
     - If "Yes", retain the uncircled species.*

2. Does the family occur at the site?
   - If "No", go to step 3.
   - If "Yes", are there one or more genera in the family that occur at the site but are not in the dataset?
     - If "No", go to step 3.
     - If "Yes", retain the uncircled species.*

3. Does the order occur at the site?
   - If "No", go to step 4.
   - If "Yes", does the dataset contain a circled species that is in the same order?
     - If "No", retain the uncircled species.*
     - If "Yes", delete the uncircled species.*

4. Does the class occur at the site?
   - If "No", go to step 5.
   - If "Yes", does the dataset contain a circled species that is in the same class?
     - If "No", retain the uncircled species.*
     - If "Yes", delete the uncircled species.*

5. Does the phylum occur at the site?
   - If "No", delete the uncircled species.*
   - If "Yes", does the dataset contain a circled species that is in the same phylum?
     - If "No", retain the uncircled species.*
     - If "Yes", delete the uncircled species.*

* = Continue the deletion process by starting at step 1 for another uncircled species unless all uncircled species in the dataset have been considered.

The species that are circled and those that are retained constitute the site-specific dataset. (An example of the deletion process is given in Figure B1.)

This deletion process is designed to ensure that:

a. Each species that occurs both in the national dataset and at the site also occurs in the site-specific dataset.

b. Each species that occurs at the site but does not occur in the national dataset is represented in the site-specific dataset by <u>all</u> species in the national dataset that are in the same genus.
c. Each genus that occurs at the site but does not occur in the national dataset is represented in the site-specific dataset by <u>all</u> genera in the national dataset that are in the same family.
d. Each order, class, and phylum that occurs both in the national dataset and at the site is represented in the site-specific dataset by the one or more species in the national dataset that are most closely related to a species that occurs at the site.

<u>D. Checking the Minimum Data Requirements</u>

The initial MDRs for the Recalculation Procedure are the same as those for the derivation of a national criterion. If a specific requirement cannot be satisfied after deletion because that kind of species does not occur at the site, a taxonomically similar species **must** be substituted in order to meet the eight MDRs:

> If no species of the kind required occurs at the site, but a species in the same order does, the MDR can only be satisfied by data for a species that occurs at the site and is in that order; if no species in the order occurs at the site, but a species in the class does, the MDR can only be satisfied by data for a species that occurs at the site and is in that class. If no species in the same class occurs at the site, but a species in the phylum does, the MDR can only be satisfied by data for a species that occurs at the site and is in that phylum. If no species in the same phylum occurs at the site, any species that occurs at the site and is not used to satisfy a different MDR can be used to satisfy the MDR. If additional data are generated using acceptable procedures (U.S. EPA 1985) and they are approved by the U.S. EPA, the Recalculation Procedure **must** be started again at step B with the addition of the new data.

If fewer than eight families of aquatic invertebrates, amphibians, and fishes occur at the site, a Species Mean Acute Value **must** be available for at least one species in each of the families and the special version of the Recalculation Procedure described on the second page of this appendix **must** be used.

<u>E. Determining the CMC and/or CCC</u>

1. Determining the FAV:
   a. If the eight family MDRs are satisfied, the site-specific FAV **must** be calculated from Genus Mean Acute Values using

the procedure described in the national aquatic life guidelines (U.S. EPA 1985).

b. If fewer than eight families of aquatic invertebrates, amphibians, and fishes occur at the site, the lowest Species Mean Acute Value that is available for a species that occurs at the site **must** be used as the FAV, as per the special version of the Recalculation Procedure described on the second page of this appendix.

2. The site-specific CMC **must** be calculated by dividing the site-specific FAV by 2. The site-specific FCV **must** be calculated by dividing the site-specific FAV by the national FACR (or by a site-specific FACR if one is derived). (Because a FACR was not used to derive the national CCC for cadmium in fresh water, the site-specific CCC equals the site-specific FCV.)
3. The calculated FAV, CMC, and/or CCC **must** be lowered, if necessary, to (1) protect an aquatic plant, invertebrate, amphibian, or fish species that is a critical species at the site, and (2) ensure that the criterion is not likely to jeopardize the continued existence of any endangered or threatened species listed under section 4 of the Endangered Species Act or result in the destruction or adverse modification of such species' critical habitat.

F. Writing the Report

The report of the results of use of the Recalculation Procedure **must** include:

1. A list of all species of aquatic invertebrates, amphibians, and fishes that are known to "occur at the site", along with the source of the information.
2. A list of all aquatic plant, invertebrate, amphibian, and fish species that are critical species at the site, including all species that occur at the site and are listed as threatened or endangered under section 4 of the Endangered Species Act.
3. A site-specific version of Table 1 from a criteria document produced by the U.S. EPA after 1984.
4. A site-specific version of Table 3 from a criteria document produced by the U.S. EPA after 1984.
5. A list of all species that were deleted.
6. The new calculated FAV, CMC, and/or CCC.
7. The lowered FAV, CMC, and/or CCC, if one or more were lowered to protect a specific species.

Reference

U.S. EPA. 1985. Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses. PB85-227049. National Technical Information Service, Springfield, VA.

Figure B1: An Example of the Deletion Process Using Three Phyla

SPECIES THAT ARE IN THE THREE PHYLA AND OCCUR AT THE SITE

Phylum	Class	Order	Family	Species
Annelida	Hirudin.	Rhynchob.	Glossiph.	Glossip. complanata
Bryozoa	(No species in this phylum occur at the site.)			
Chordata	Osteich.	Cyprinif.	Cyprinid.	Carassius auratus
Chordata	Osteich.	Cyprinif.	Cyprinid.	Notropis anogenus
Chordata	Osteich.	Cyprinif.	Cyprinid.	Phoxinus eos
Chordata	Osteich.	Cyprinif.	Catostom.	Carpiodes carpio
Chordata	Osteich.	Salmonif.	Osmerida.	Osmerus mordax
Chordata	Osteich.	Percifor.	Centrarc.	Lepomis cyanellus
Chordata	Osteich.	Percifor.	Centrarc.	Lepomis humilis
Chordata	Amphibia	Caudata	Ambystom.	Ambystoma gracile

SPECIES THAT ARE IN THE THREE PHYLA AND IN THE NATIONAL DATASET

Phylum	Class	Order	Family	Species	Code
Annelida	Oligoch.	Haplotax.	Tubifici.	Tubifex tubifex	P
Bryozoa	Phylact.	---	Lophopod.	Lophopod. carteri	D
Chordata	Cephala.	Petromyz.	Petromyz.	Petromyzon marinus	D
Chordata	Osteich.	Cyprinif.	Cyprinid.	Carassius auratus	S
Chordata	Osteich.	Cyprinif.	Cyprinid.	Notropis hudsonius	G
Chordata	Osteich.	Cyprinif.	Cyprinid.	Notropis stramineus	G
Chordata	Osteich.	Cyprinif.	Cyprinid.	Phoxinus eos	S
Chordata	Osteich.	Cyprinif.	Cyprinid.	Phoxinus oreas	D
Chordata	Osteich.	Cyprinif.	Cyprinid.	Tinca tinca	D
Chordata	Osteich.	Cyprinif.	Catostom.	Ictiobus bubalus	F
Chordata	Osteich.	Salmonif.	Salmonid.	Oncorhynchus mykiss	O
Chordata	Osteich.	Percifor.	Centrarc.	Lepomis cyanellus	S
Chordata	Osteich.	Percifor.	Centrarc.	Lepomis macrochirus	G
Chordata	Osteich.	Percifor.	Percidae	Perca flavescens	D
Chordata	Amphibia	Anura	Pipidae	Xenopus laevis	C

Explanations of Codes:

- S = retained because this Species occurs at the site.
- G = retained because there is a species in this Genus that occurs at the site but not in the national dataset.
- F = retained because there is a genus in this Family that occurs at the site but not in the national dataset.
- O = retained because this Order occurs at the site and is not represented by a lower taxon.
- C = retained because this Class occurs at the site and is not represented by a lower taxon.
- P = retained because this Phylum occurs at the site and is not represented by a lower taxon.
- D = deleted because this species does not satisfy any of the requirements for retaining species.

Appendix C: Guidance Concerning the Use of "Clean Techniques" and QA/QC when Measuring Trace Metals

Note: This version of this appendix contains more information than the version that was Appendix B of Prothro (1993).

Recent information (Shiller and Boyle 1987; Windom et al. 1991) has raised questions concerning the quality of reported concentrations of trace metals in both fresh and salt (estuarine and marine) surface waters. A lack of awareness of true ambient concentrations of metals in fresh and salt surface waters can be both a cause and a result of the problem. The ranges of dissolved metals that are typical in surface waters of the United States away from the immediate influence of discharges (Bruland 1983; Shiller and Boyle 1985,1987; Trefry et al. 1986; Windom et al. 1991) are:

Metal	Salt water (µg/L)	Fresh water (µg/L)
Cadmium	0.01 to 0.2	0.002 to 0.08
Copper	0.1 to 3.	0.4 to 4.
Lead	0.01 to 1.	0.01 to 0.19
Nickel	0.3 to 5.	1. to 2.
Silver	0.005 to 0.2	-------------
Zinc	0.1 to 15.	0.03 to 5.

The U.S. EPA (1983,1991) has published analytical methods for monitoring metals in waters and wastewaters, but these methods are inadequate for determination of ambient concentrations of some metals in some surface waters. Accurate and precise measurement of these low concentrations requires appropriate attention to seven areas:

1. Use of "clean techniques" during collecting, handling, storing, preparing, and analyzing samples to avoid contamination.
2. Use of analytical methods that have sufficiently low detection limits.
3. Avoidance of interference in the quantification (instrumental analysis) step.
4. Use of blanks to assess contamination.
5. Use of matrix spikes (sample spikes) and certified reference materials (CRMs) to assess interference and contamination.
6. Use of replicates to assess precision.
7. Use of certified standards.

In a strict sense, the term "clean techniques" refers to techniques that reduce contamination and enable the accurate and precise measurement of trace metals in fresh and salt surface waters. In a broader sense, the term also refers to related issues concerning detection limits, quality control, and quality assurance. Documenting data quality demonstrates the amount of confidence that can be placed in the data, whereas increasing the sensitivity of methods reduces the problem of deciding how to interpret results that are reported to be below detection limits.

<u>This appendix is written for those analytical laboratories that want guidance concerning ways to lower detection limits, increase accuracy, and/or increase precision.</u> The ways to achieve these goals are to increase the sensitivity of the analytical methods, decrease contamination, and decrease interference. Ideally, validation of a procedure for measuring concentrations of metals in surface water requires demonstration that agreement can be obtained using completely different procedures beginning with the sampling step and continuing through the quantification step (Bruland et al. 1979), but few laboratories have the resources to compare two different procedures. Laboratories can, however, (a) use techniques that others have found useful for improving detection limits, accuracy, and precision, and (b) document data quality through use of blanks, spikes, CRMs, replicates, and standards.

<u>Nothing contained or not contained in this appendix adds to or subtracts from any regulatory requirement set forth in other EPA documents concerning analyses of metals.</u> A WER can be acceptably determined without the use of clean techniques as long as the detection limits, accuracy, and precision are acceptable. No QA/QC requirements beyond those that apply to measuring metals in effluents are necessary for the determination of WERs. The word "must" is not used in this appendix. Some items, however, are considered so important by analytical chemists who have worked to increase accuracy and precision and lower detection limits in trace-metal analysis that "**should**" is in bold print to draw attention to the item. Most such items are emphasized because they have been found to have received inadequate attention in some laboratories performing trace-metal analyses.

In general, in order to achieve accurate and precise measurement of a particular concentration, both the detection limit and the blanks should be less than one-tenth of that concentration. Therefore, the term "metal-free" can be interpreted to mean that the total amount of contamination that occurs during sample collection and processing (e.g., from gloves, sample containers, labware, sampling apparatus, cleaning solutions, air, reagents, etc.) is sufficiently low that blanks are less than one-tenth of the lowest concentration that needs to be measured.

Atmospheric particulates can be a major source of contamination (Moody 1982; Adeloju and Bond 1985). The term "class-100" refers to a specification concerning the amount of particulates in air (Moody 1982); although the specification says nothing about the composition of the particulates, generic control of particulates can greatly reduce trace-metal blanks. Except during collection of samples, initial cleaning of equipment, and handling of samples containing high concentrations of metals, all handling of samples, sample containers, labware, and sampling apparatus should be performed in a class-100 bench, room, or glove box.

Neither the "ultraclean techniques" that might be necessary when trace analyses of mercury are performed nor safety in analytical laboratories is addressed herein. Other documents should be consulted if one or both of these topics are of concern.

Avoiding contamination by use of "clean techniques"

Measurement of trace metals in surface waters should take into account the potential for contamination during each step in the process. Regardless of the specific procedures used for collection, handling, storage, preparation (digestion, filtration, and/or extraction), and quantification (instrumental analysis), the general principles of contamination control should be applied. Some specific recommendations are:

a. Powder-free (non-talc, class-100) latex, polyethylene, or polyvinyl chloride (PVC, vinyl) gloves **should** be worn during all steps from sample collection to analysis. (Talc seems to be a particular problem with zinc; gloves made with talc cannot be decontaminated sufficiently.) Gloves should only contact surfaces that are metal-free; gloves should be changed if even suspected of contamination.
b. The acid used to acidify samples for preservation and digestion and to acidify water for final cleaning of labware, sampling apparatus, and sample containers **should** be metal-free. The quality of the acid used should be better than reagent-grade. Each lot of acid **should** be analyzed for the metal(s) of interest before use.
c. The water used to prepare acidic cleaning solutions and to rinse labware, sample containers, and sampling apparatus may be prepared by distillation, deionization, or reverse osmosis, and **should** be demonstrated to be metal-free.
d. The work area, including bench tops and hoods, should be cleaned (e.g., washed and wiped dry with lint-free, class-100 wipes) frequently to remove contamination.
e. All handling of samples in the laboratory, including filtering and analysis, **should** be performed in a class-100 clean bench or a glove box fed by particle-free air or nitrogen; ideally the clean bench or glove box should be located within a class-100 clean room.
f. Labware, reagents, sampling apparatus, and sample containers **should** never be left open to the atmosphere; they should be stored in a class-100 bench, covered with plastic wrap, stored in a plastic box, or turned upside down on a clean surface. Minimizing the time between cleaning and using will help minimize contamination.

g. Separate sets of sample containers, labware, and sampling apparatus should be dedicated for different kinds of samples, e.g., surface water samples, effluent samples, etc.
h. To avoid contamination of clean rooms, samples that contain very high concentrations of metals and do not require use of "clean techniques" **should not** be brought into clean rooms.
i. Acid-cleaned plastic, such as high-density polyethylene (HDPE), low-density polyethylene (LDPE), or a fluoroplastic, **should** be the only material that ever contacts a sample, except possibly during digestion for the total recoverable measurement.
   1. Total recoverable samples can be digested in some plastic containers.
   2. HDPE and LDPE might not be acceptable for mercury.
   3. Even if acidified, samples and standards containing silver should be in amber containers.
j. All labware, sample containers, and sampling apparatus **should** be acid-cleaned before use or reuse.
   1. Sample containers, sampling apparatus, tubing, membrane filters, filter assemblies, and other labware **should** be soaked in acid until metal-free. The amount of cleaning necessary might depend on the amount of contamination and the length of time the item will be in contact with samples. For example, if an acidified sample will be stored in a sample container for three weeks, ideally the container should have been soaked in an acidified metal-free solution for at least three weeks.
   2. It might be desirable to perform initial cleaning, for which reagent-grade acid may be used, before the items are taken into a clean room. For most metals, items should be either (a) soaked in 10 percent concentrated nitric acid at 50°C for at least one hour, or (b) soaked in 50 percent concentrated nitric acid at room temperature for at least two days; for arsenic and mercury, soaking for up to two weeks at 50°C in 10 percent concentrated nitric acid might be required. For plastics that might be damaged by strong nitric acid, such as polycarbonate and possibly HDPE and LDPE, soaking in 10 percent concentrated hydrochloric acid, either in place of or before soaking in a nitric acid solution, might be desirable.
   3. Chromic acid **should not** be used to clean items that will be used in analysis of metals.
   4. Final soaking and cleaning of sample containers, labware, and sampling apparatus **should** be performed in a class-100 clean room using metal-free acid and water. The solution in an acid bath **should** be analyzed periodically to demonstrate that it is metal-free.
k. Labware, sampling apparatus, and sample containers **should** be stored appropriately after cleaning:
   1. After the labware and sampling apparatus are cleaned, they may be stored in a clean room in a weak acid bath prepared using metal-free acid and water. Before use, the items

should be rinsed at least three times with metal-free water. After the final rinse, the items should be moved immediately, with the open end pointed down, to a class-100 clean bench. Items may be dried on a class-100 clean bench; items **should not** be dried in an oven or with laboratory towels. The sampling apparatus should be assembled in a class-100 clean room or bench and double-bagged in metal-free polyethylene zip-type bags for transport to the field; new bags are usually metal-free.

2. After sample containers are cleaned, they should be filled with metal-free water that has been acidified to a pH of 2 with metal-free nitric acid (about 0.5 mL per liter) for storage until use.

l. Labware, sampling apparatus, and sample containers **should** be rinsed and not rinsed with sample as necessary to prevent high and low bias of analytical results because acid-cleaned plastic will sorb some metals from unacidified solutions.

1. Because samples for the dissolved measurement are not acidified until after filtration, all sampling apparatus, sample containers, labware, filter holders, membrane filters, etc., that contact the sample before or during filtration **should** be rinsed with a portion of the solution and then that portion discarded.
2. For the total recoverable measurement, labware, etc., that contact the sample <u>only</u> before it is acidified **should** be rinsed with sample, whereas items that contact the sample after it is acidified **should not** be rinsed. For example, the sampling apparatus should be rinsed because the sample will not be acidified until it is in a sample container, but the sample container should not be rinsed <u>if</u> the sample will be acidified in the sample container.
3. If the total recoverable and dissolved measurements are to be performed on the same sample (rather than on two samples obtained at the same time and place), all the apparatus and labware, including the sample container, should be rinsed before the sample is placed in the sample container; then an unacidified aliquot should be removed for the total recoverable measurement (and acidified, digested, etc.) and an unacidified aliquot should be removed for the dissolved measurement (and filtered, acidified, etc.) (If a container is rinsed and filled with sample and an unacidified aliquot is removed for the dissolved measurement and then the solution in the container is acidified before removal of an aliquot for the total recoverable measurement, the resulting measured total recoverable concentration might be biased high because the acidification might desorb metal that had been sorbed onto the walls of the sample container; the amount of bias will depend on the relative volumes involved and on the amount of sorption and desorption.)

m. Field samples **should** be collected in a manner that eliminates the potential for contamination from sampling platforms, probes, etc. Exhaust from boats and the direction of wind and water currents should be taken into account. The people who collect the samples **should** be specifically trained on how to collect field samples. After collection, all handling of samples in the field that will expose the sample to air **should** be performed in a portable class-100 clean bench or glove box.

n. Samples **should** be acidified (after filtration if dissolved metal is to be measured) to a pH of less than 2, except that the pH **should** be less than 1 for mercury. Acidification should be done in a clean room or bench, and so it might be desirable to wait and acidify samples in a laboratory rather than in the field. If samples are acidified in the field, metal-free acid can be transported in plastic bottles and poured into a plastic container from which acid can be removed and added to samples using plastic pipettes. Alternatively, plastic automatic dispensers can be used.
o. Such things as probes and thermometers **should not** be put in samples that are to be analyzed for metals. In particular, pH electrodes and mercury-in-glass thermometers **should not** be used if mercury is to be measured. If pH is measured, it **should** be done on a separate aliquot.
p. Sample handling should be minimized. For example, instead of pouring a sample into a graduated cylinder to measure the volume, the sample can be weighed after being poured into a tared container, which is less likely to be subject to error than weighing the container from which the sample is poured. (For saltwater samples, the salinity or density should be taken into account if weight is converted to volume.)
q. Each reagent used **should** be verified to be metal-free. If metal-free reagents are not commercially available, removal of metals will probably be necessary.
r. For the total recoverable measurement, samples should be digested in a class-100 bench, not in a metallic hood. If feasible, digestion should be done in the sample container by acidification and heating.
s. The longer the time between collection and analysis of samples, the greater the chance of contamination, loss, etc.
t. Samples should be stored in the dark, preferably between 0 and 4°C with no air space in the sample container.

Achieving low detection limits

a. Extraction of the metal from the sample can be extremely useful if it simultaneously concentrates the metal and eliminates potential matrix interferences. For example, ammonium 1-pyrrolidinedithiocarbamate and/or diethylammonium diethyldithiocarbamate can extract cadmium, copper, lead, nickel, and zinc (Bruland et al. 1979; Nriagu et al. 1993).
b. The detection limit should be less than ten percent of the lowest concentration that is to be measured.

Avoiding interferences

a. Potential interferences **should** be assessed for the specific instrumental analysis technique used and for each metal to be measured.
b. If direct analysis is used, the salt present in high-salinity saltwater samples is likely to cause interference in most instrumental techniques.
c. As stated above, extraction of the metal from the sample is particularly useful because it simultaneously concentrates the metal and eliminates potential matrix interferences.

Using blanks to assess contamination

a. A laboratory (procedural, method) blank consists of filling a sample container with analyzed metal-free water and processing (filtering, acidifying, etc.) the water through the laboratory procedure in exactly the same way as a sample. A laboratory blank **should** be included in each set of ten or fewer samples to check for contamination in the laboratory, and **should** contain less than ten percent of the lowest concentration that is to be measured. Separate laboratory blanks **should** be processed for the total recoverable and dissolved measurements, if both measurements are performed.
b. A field (trip) blank consists of filling a sample container with analyzed metal-free water in the laboratory, taking the container to the site, processing the water through tubing, filter, etc., collecting the water in a sample container, and acidifying the water the same as a field sample. A field blank **should** be processed for each sampling trip. Separate field blanks **should** be processed for the total recoverable measurement and for the dissolved measurement, if filtrations are performed at the site. Field blanks **should** be processed in the laboratory the same as laboratory blanks.

Assessing accuracy

a. A calibration curve **should** be determined for each analytical run and the calibration should be checked about every tenth sample. Calibration solutions **should** be traceable back to a certified standard from the U.S. EPA or the National Institute of Science and Technology (NIST).
b. A blind standard or a blind calibration solution **should** be included in each group of about twenty samples.
c. At least one of the following **should** be included in each group of about twenty samples:
   1. A matrix spike (spiked sample; the method of known additions).

2. A CRM, if one is available in a matrix that closely approximates that of the samples. Values obtained for the CRM **should** be within the published values.

The concentrations in blind standards and solutions, spikes, and CRMs **should not** be more than 5 times the median concentration expected to be present in the samples.

Assessing precision

a. A sampling replicate **should** be included with each set of samples collected at each sampling location.
b. If the volume of the sample is large enough, replicate analysis of at least one sample **should** be performed along with each group of about ten samples.

Special considerations concerning the dissolved measurement

Whereas total recoverable measurements are especially subject to contamination during digestion, dissolved measurements are subject to both loss and contamination during filtration.

a. Because acid-cleaned plastic sorbs metal from unacidified solutions and because samples for the dissolved measurement are not acidified before filtration, all sampling apparatus, sample containers, labware, filter holders, and membrane filters that contact the sample before or during filtration **should** be conditioned by rinsing with a portion of the solution and discarding that portion.
b. Filtrations **should** be performed using acid-cleaned plastic filter holders and acid-cleaned membrane filters. Samples **should not** be filtered through glass fiber filters, even if the filters have been cleaned with acid. If positive-pressure filtration is used, the air or gas **should** be passed through a 0.2-μm in-line filter; if vacuum filtration is used, it **should** be performed on a class-100 bench.
c. Plastic filter holders **should** be rinsed and/or dipped between filtrations, but they do not have to be soaked between filtrations if all the samples contain about the same concentrations of metal. It is best to filter samples from low to high concentrations. A membrane filter **should not** be used for more than one filtration. After each filtration, the membrane filter **should** be removed and discarded, and the filter holder **should** be either rinsed with metal-free water or dilute acid and dipped in a metal-free acid bath or rinsed at least twice with metal-free dilute acid; finally, the filter holder **should** be rinsed at least twice with metal-free water.
d. For each sample to be filtered, the filter holder and membrane filter **should** be conditioned with the sample, i.e., an initial portion of the sample **should** be filtered and discarded.

The accuracy and precision of the dissolved measurement **should** be assessed periodically. A large volume of a buffered solution (such as aerated 0.05 N sodium bicarbonate for analyses in fresh water and a combination of sodium bicarbonate and sodium chloride for analyses in salt water) should be spiked so that the concentration of the metal of interest is in the range of the low concentrations that are to be measured. Sufficient samples should be taken alternately for (a) acidification in the same way as after filtration in the dissolved method and (b) filtration and acidification using the procedures specified in the dissolved method until ten samples have been processed in each way. The concentration of metal in each of the twenty samples should then be determined using the same analytical procedure. The means of the two groups of ten measurements should be within 10 percent, and the coefficient of variation for each group of ten should be less than 20 percent. Any values deleted as outliers **should** be acknowledged.

Reporting results

To indicate the quality of the data, reports of results of measurements of the concentrations of metals **should** include a description of the blanks, spikes, CRMs, replicates, and standards that were run, the number run, and the results obtained. All values deleted as outliers **should** be acknowledged.

Additional information

The items presented above are some of the important aspects of "clean techniques"; some aspects of quality assurance and quality control are also presented. This is not a definitive treatment of these topics; additional information that might be useful is available in such publications as Patterson and Settle (1976), Zief and Mitchell (1976), Bruland et al. (1979), Moody and Beary (1982), Moody (1982), Bruland (1983), Adeloju and Bond (1985), Berman and Yeats (1985), Byrd and Andreae (1986), Taylor (1987), Sakamoto-Arnold (1987), Tramontano et al. (1987), Puls and Barcelona (1989), Windom et al. (1991), U.S. EPA (1992), Horowitz et al. (1992), and Nriagu et al. (1993).

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Appendix D: Relationships between WERs and the Chemistry and Toxicology of Metals

The aquatic toxicology of metals is complex in part because the chemistry of metals in water is complex. Metals usually exist in surface water in various combinations of particulate and dissolved forms, some of which are toxic and some of which are nontoxic. In addition, all toxic forms of a metal are not necessarily equally toxic, and various water quality characteristics can affect the relative concentrations and/or toxicities of some of the forms.

The toxicity of a metal has sometimes been reported to be proportional to the concentration or activity of a specific species of the metal. For example, Allen and Hansen (1993) summarized reports by several investigators that the toxicity of copper is related to the free cupric ion, but other data do not support a correlation (Erickson 1993a). For example, Borgmann (1983), Chapman and McCrady (1977), and French and Hunt (1986) found that toxicity expressed on the basis of cupric ion activity varied greatly with pH, and Cowan et al. (1986) concluded that at least one of the copper hydroxide species is toxic. Further, chloride and sulfate salts of calcium, magnesium, potassium, and sodium affect the toxicity of the cupric ion (Nelson et al. 1986). Similarly for aluminum, Wilkinson et al. (1993) concluded that "mortality was best predicted not by the free Al^{3+} activity but rather as a function of the sum $\Sigma([Al^{3+}] + [AlF^{2+}])$" and that "no longer can the reduction of Al toxicity in the presence of organic acids be interpreted simply as a consequence of the decrease in the free Al^{3+} concentration".

Until a model has been demonstrated to explain the quantitative relationship between chemical and toxicological measurements, aquatic life criteria should be established in an environmentally conservative manner with provision for site-specific adjustment. Criteria should be expressed in terms of feasible analytical measurements that provide the necessary conservatism without substantially increasing the cost of implementation and site-specific adjustment. Thus current aquatic life criteria for metals are expressed in terms of the total recoverable measurement and/or the dissolved measurement, rather than a measurement that would be more difficult to perform and would still require empirical adjustment. The WER is operationally defined in terms of chemical and toxicological measurements to allow site-specific adjustments that account for differences between the toxicity of a metal in laboratory dilution water and in site water.

Forms of Metals

Even if the relationship of toxicity to the forms of metals is not understood well enough to allow setting site-specific water quality criteria without using empirical adjustments, appropriate use and interpretation of WERs requires an understanding of how changes in the relative concentrations of different forms of a metal might affect toxicity. Because WERs are defined on the basis of relationships between measurements of toxicity and measurements of total recoverable and/or dissolved metal, the toxicologically relevant distinction is between the forms of the metal that are toxic and nontoxic whereas the chemically relevant distinction is between the forms that are dissolved and particulate. "Dissolved metal" is defined here as "metal that passes through either a 0.45-μm or a 0.40-μm membrane filter" and "particulate metal" is defined as "total recoverable metal minus dissolved metal". Metal that is in or on particles that pass through the filter is operationally defined as "dissolved".

In addition, some species of metal can be converted from one form to another. Some conversions are the result of reequilibration in response to changes in water quality characteristics whereas others are due to such fate processes as oxidation of sulfides and/or organic matter. Reequilibration usually occurs faster than fate processes and probably results in any rapid changes that are due to effluent mixing with receiving water or changes in pH at a gill surface. To account for rapid changes due to reequilibration, the terms "labile" and "refractory" will be used herein to denote metal species that do and do not readily convert to other species when in a nonequilibrium condition, with "readily" referring to substantial progression toward equilibrium in less than about an hour. Although the toxicity and lability of a form of a metal are not merely yes/no properties, but rather involve gradations, a simple classification scheme such as this should be sufficient to establish the principles regarding how WERs are related to various operationally defined forms of metal and how this affects the determination and use of WERs.

Figure D1 presents the classification scheme that results from distinguishing forms of metal based on analytical methodology, toxicity tests, and lability, as described above. Metal that is not measured by the total recoverable measurement is assumed to be sufficiently nontoxic and refractory that it will not be further considered here. Allowance is made for toxicity due to particulate metal because some data indicate that particulate metal might contribute to toxicity and bioaccumulation, although other data imply that little or no toxicity can be ascribed to particulate metal (Erickson 1993b). Even if the toxicity of particulate metal is not negligible in a particular situation, a dissolved criterion will not be underprotective if the dissolved criterion was derived using a dissolved WER (see below) or if there are sufficient compensating factors.

Figure D1: A Scheme for Classifying Forms of Metal in Water

- Total recoverable metal
  - Dissolved
    - Nontoxic
      - Labile
      - Refractory
    - Toxic
      - Labile
  - Particulate
    - Nontoxic
      - Labile
      - Refractory
    - Toxic
      - Labile
- Metal not measured by the total recoverable measurement

Not only can some changes in water quality characteristics shift the relative concentrations of toxic and nontoxic labile species of a metal, some changes in water quality can also increase or decrease the toxicities of the toxic species of a metal and/or the sensitivities of aquatic organisms. Such changes might be caused by (a) a change in ionic strength that affects the activity of toxic species of the metal in water, (b) a physiological effect whereby an ion affects the permeability of a membrane and thereby alters both uptake and apparent toxicity, and (c) toxicological additivity, synergism, or antagonism due to effects within the organism.

Another possible complication is that a form of metal that is toxic to one aquatic organism might not be toxic to another. Although such differences between organisms have not been demonstrated, the possibility cannot be ruled out.

The Importance of Lability

The only common metal measurement that can be validly extrapolated from the effluent and the upstream water to the downstream water merely by taking dilution into account is the total recoverable measurement. A major reason this measurement is so useful is because it is the only measurement that obeys the law of mass balance (i.e., it is the only measurement that is conservative). Other metal measurements usually do not obey the law of mass balance because they measure some, but not all, of the labile species of metals. A measurement of refractory metal would be conservative in terms of changes in water quality characteristics, but not necessarily in regards to fate processes; such a measurement has not been developed, however.

Permit limits apply to effluents, whereas water quality criteria apply to surface waters. If permit limits and water quality criteria are both expressed in terms of total recoverable metal, extrapolations from effluent to surface water only need to take dilution into account and can be performed as mass balance calculations. If either permit limits or water quality criteria or both are expressed in terms of any other metal measurement, lability needs to be taken into account, even if both are expressed in terms of the same measurement.

Extrapolations concerning labile species of metals from effluent to surface water depend to a large extent on the differences between the water quality characteristics of the effluent and those of the surface water. Although equilibrium models of the speciation of metals can provide insight, the interactions are too complex to be able to make useful nonempirical extrapolations from a wide variety of effluents to a wide variety of surface waters of either (a) the speciation of the metal or (b) a metal measurement other than total recoverable.

Empirical extrapolations can be performed fairly easily and the most common case will probably occur when permit limits are based on the total recoverable measurement but water quality criteria are based on the dissolved measurement. The empirical extrapolation is intended to answer the question "What percent of the total recoverable metal in the effluent becomes dissolved in the downstream water?" This question can be answered by:

a. Collecting samples of effluent and upstream water.
b. Measuring total recoverable metal and dissolved metal in both samples.
c. Combining aliquots of the two samples in the ratio of the flows when the samples were obtained and mixing for an appropriate period of time under appropriate conditions.
d. Measuring total recoverable metal and dissolved metal in the mixture.

An example is presented in Figure D2. This percentage cannot be extrapolated from one metal to another or from one effluent to another. The data needed to calculate the percentage will be obtained each time a WER is determined using simulated downstream water if both dissolved and total recoverable metal are measured in the effluent, upstream water, and simulated downstream water.

The interpretation of the percentage is not necessarily as straightforward as might be assumed. For example, some of the metal that is dissolved in the upstream water might sorb onto particulate matter in the effluent, which can be viewed as a detoxification of the upstream water by the effluent. Regardless of the interpretation, the described procedure provides a simple way of relating the total recoverable concentration in the effluent to the concentration of concern in the downstream water. Because this empirical extrapolation can be used with any analytical measurement that is chosen as the basis for expression of aquatic life criteria, use of the total recoverable measurement to express permit limits on effluents does not place any restrictions on which analytical measurement can be used to express criteria. Further, even if both criteria and permit limits are expressed in terms of a measurement such as dissolved metal, an empirical extrapolation would still be necessary because dissolved metal is not likely to be conservative from effluent to downstream water.

Merits of Total Recoverable and Dissolved WERs and Criteria

A WER is operationally defined as the value of an endpoint obtained with a toxicity test using site water divided by the value of the same endpoint obtained with the same toxicity test using a laboratory dilution water. Therefore, just as aquatic life criteria can be expressed in terms of either the total recoverable measurement or the dissolved measurement, so can WERs. A pair of side-by-side toxicity tests can produce both a total recoverable WER and a dissolved WER if the metal in the test solutions in both of the tests is measured using both methods. A total recoverable WER is obtained by dividing endpoints that were calculated on the basis of total recoverable metal, whereas a dissolved WER is obtained by dividing endpoints that were calculated on the basis of dissolved metal. Because of the way they are determined, a total recoverable WER is used to calculate a total recoverable site-specific criterion from a national, state, or recalculated aquatic life criterion that is expressed using the total recoverable measurement, whereas a dissolved WER is used to calculate a dissolved site-specific criterion from a national, state, or recalculated criterion that is expressed in terms of the dissolved measurement.

In terms of the classification scheme given in Figure D1, the basic relationship between a total recoverable national water quality criterion and a total recoverable WER is:

- A total recoverable criterion treats all the toxic and nontoxic metal in the site water as if its average toxicity were the same as the average toxicity of all the toxic and nontoxic metal in the toxicity tests in laboratory dilution water on which the criterion is based.
- A total recoverable WER is a measurement of the actual ratio of the average toxicities of the total recoverable metal and replaces the assumption that the ratio is 1.

Similarly, the basic relationship between a dissolved national criterion and a dissolved WER is:

- A dissolved criterion treats all the toxic and nontoxic dissolved metal in the site water as if its average toxicity were the same as the average toxicity of all the toxic and nontoxic dissolved metal in the toxicity tests in laboratory dilution water on which the criterion is based.
- A dissolved WER is a measurement of the actual ratio of the average toxicities of the dissolved metal and replaces the assumption that the ratio is 1.

In both cases, use of a criterion without a WER involves measurement of toxicity in laboratory dilution water but only prediction of toxicity in site water, whereas use of a criterion with a WER involves measurement of toxicity in both laboratory dilution water and site water.

When WERs are used to derive site-specific criteria, the total recoverable and dissolved approaches are inherently consistent. They are consistent because the toxic effects caused by the metal in the toxicity tests do not depend on what chemical measurements are performed; the same number of organisms are killed in the acute lethality tests regardless of what, if any, measurements of the concentration of the metal are made. The only difference is the chemical measurement to which the toxicity is referenced. Dissolved WERs can be derived from the same pairs of toxicity tests from which total recoverable WERs are derived, if the metal in the tests is measured using both the total recoverable and dissolved measurements. Both approaches start at the same place (i.e., the amount of toxicity observed in laboratory dilution water) and end at the same place (i.e., the amount of toxicity observed in site water). The combination of a total recoverable criterion and WER accomplish the same thing as the combination of a dissolved criterion and WER. By extension, whenever a criterion and a WER based on the same measurement of the metal are used together, they will end up at the same place. Because use of a total recoverable criterion with a total recoverable WER ends up at exactly the same place as use of a dissolved criterion with a dissolved WER, whenever one WER is determined, both should be determined to allow (a) a check on the analytical chemistry, (b) use of the inherent internal consistency to check that the data are used correctly, and (c) the option of using either approach in the derivation of permit limits.

An examination of how the two approaches (the total recoverable approach and the dissolved approach) address the four relevant forms of metal (toxic and nontoxic particulate metal and toxic and nontoxic dissolved metal) in laboratory dilution water and in site water further explains why the two approaches are inherently consistent. Here, only the way in which the two approaches address each of the four forms of metal in site water will be considered:

a. Toxic dissolved metal:

This form contributes to the toxicity of the site water and is measured by both chemical measurements. If this is the only form of metal present, the two WERs will be the same.

b. Nontoxic dissolved metal:

This form does not contribute to the toxicity of the site water, but it is measured by both chemical measurements. If this is the only form of metal present, the two WERs will be the same. (Nontoxic dissolved metal can be the only form present, however, only if all of the nontoxic dissolved metal present is refractory. If any labile nontoxic dissolved metal is present, equilibrium will require that some toxic dissolved metal also be present.)

c. Toxic particulate metal:

This form contributes to the toxicological measurement in both approaches; it is measured by the total recoverable measurement, but not by the dissolved measurement. Even though it is not measured by the dissolved measurement, its presence is accounted for in the dissolved approach because it increases the toxicity of the site water and thereby decreases the dissolved WER. It is accounted for because it makes the dissolved metal appear to be more toxic than it is. Most toxic particulate metal is probably not toxic when it is particulate; it becomes toxic when it is dissolved at the gill surface or in the digestive system; in the surface water, however, it is measured as particulate metal.

d. Nontoxic particulate metal:

This form does not contribute to the toxicity of the site water; it is measured by the total recoverable measurement, but not by the dissolved measurement. Because it is measured by the total recoverable measurement, but not by the dissolved measurement, it causes the total recoverable WER to be higher than the dissolved WER.

In addition to dealing with the four forms of metal similarly, the WERs used in the two approaches comparably take synergism, antagonism, and additivity into account. Synergism and additivity in the site water increase its toxicity and therefore decrease the WER; in contrast, antagonism in the site water decreases toxicity and increases the WER.

Each of the four forms of metal is appropriately taken into account because use of the WERs makes the two approaches internally consistent. In addition, although experimental variation will cause the measured WERs to deviate from the actual WERs, the measured WERs will be internally consistent with the data from which they were generated. If the percent dissolved is the same at the test endpoint in the two waters, the two WERs will be the same. If the percent of the total recoverable metal that is dissolved in laboratory dilution water is less than 100 percent, changing from the total recoverable measurement to the dissolved measurement will lower the criterion but it will comparably lower the denominator in the WER, thus increasing the WER. If the percent of the total recoverable metal that is dissolved in the site water is less than 100 percent, changing from the total recoverable measurement to the dissolved measurement will lower the concentration in the site water that is to be compared with the criterion, but it also lowers the numerator in the WER, thus lowering the WER. Thus when WERs are used to adjust criteria, the total recoverable approach and the dissolved approach result in the same interpretations of concentrations in the site water (see Figure D3) and in the same maximum acceptable concentrations in effluents (see Figure D4).

Thus, if WERs are based on toxicity tests whose endpoints equal the CMC or CCC and if both approaches are used correctly, the two measurements will produce the same results because each WER is based on measurements on the site water and then the WER is used to calculate the site-specific criterion that applies to the site water when the same chemical measurement is used to express the site-specific criterion. The equivalency of the two approaches applies if they are based on the same sample of site water. When they are applied to multiple samples, the approaches can differ depending on how the results from replicate samples are used:

a. If an appropriate averaging process is used, the two will be equivalent.
b. If the lowest value is used, the two approaches will probably be equivalent only if the lowest dissolved WER and the lowest total recoverable WER were obtained using the same sample of site water.

There are several advantages to using a dissolved criterion even when a dissolved WER is not used. In some situations use of a dissolved criterion to interpret results of measurements of the concentration of dissolved metal in site water might demonstrate that there is no need to determine either a total recoverable WER or a dissolved WER. This would occur when so much of the total recoverable metal was nontoxic particulate metal that even though the total recoverable criterion was exceeded, the corresponding dissolved criterion was not exceeded. The particulate metal might come from an effluent, a resuspension event, or runoff that washed particulates into the body of water. In such a situation the total recoverable WER would also show that the site-specific criterion was not exceeded, but there would be no need to determine a WER if the criterion were expressed on the basis of the dissolved measurement. If the variation over time in the concentration of particulate metal is much greater than the variation in the concentration of dissolved metal, both the total recoverable concentration and the total recoverable WER are likely to vary so much over time that a dissolved criterion would be much more useful than a total recoverable criterion.

Use of a dissolved criterion without a dissolved WER has three disadvantages, however:

1. Nontoxic dissolved metal in the site water is treated as if it is toxic.
2. Any toxicity due to particulate metal in the site water is ignored.
3. Synergism, antagonism, and additivity in the site water are not taken into account.

Use of a dissolved criterion with a dissolved WER overcomes all three problems. For example, if (a) the total recoverable concentration greatly exceeds the total recoverable criterion, (b) the dissolved concentration is below the dissolved criterion, and (c) there is concern about the possibility of toxicity of particulate metal, the determination of a dissolved WER would demonstrate whether toxicity due to particulate metal is measurable.

Similarly, use of a total recoverable criterion without a total recoverable WER has three comparable disadvantages:

1. Nontoxic dissolved metal in site water is treated as if it is toxic.
2. Nontoxic particulate metal in site water is treated as if it is toxic.
3. Synergism, antagonism, and additivity in site water are not taken into account.

Use of a total recoverable criterion with a total recoverable WER overcomes all three problems. For example, determination of a total recoverable WER would prevent nontoxic particulate metal (as well as nontoxic dissolved metal) in the site water from being treated as if it is toxic.

Relationships between WERs and the Forms of Metals

Probably the best way to understand what WERs can and cannot do is to understand the relationships between WERs and the forms of metals. A WER is calculated by dividing the concentration of a metal that corresponds to a toxicity endpoint in a site water by the concentration of the same metal that corresponds to the same toxicity endpoint in a laboratory dilution water. Therefore, using the classification scheme given in Figure D1:

$$WER = \frac{R_S + N_S + T_S + \Delta N_S + \Delta T_S}{R_L + N_L + T_L + \Delta N_L + \Delta T_L} .$$

The subscripts "S" and "L" denote site water and laboratory dilution water, respectively, and:

R = the concentration of Refractory metal in a water. (By definition, all refractory metal is nontoxic metal.)

N = the concentration of Nontoxic labile metal in a water.

T = the concentration of Toxic labile metal in a water.

ΔN = the concentration of metal added during a WER determination that is Nontoxic labile metal after it is added.

ΔT = the concentration of metal added during a WER determination that is Toxic labile metal after it is added.

For a total recoverable WER, each of these five concentrations includes both particulate and dissolved metal, if both are present; for a dissolved WER only dissolved metal is included.

Because the two side-by-side tests use the same endpoint and are conducted under identical conditions with comparable test organisms, $T_S + \Delta T_S = T_L + \Delta T_L$ when the toxic species of the metal are equally toxic in the two waters. If a difference in water quality causes one or more of the toxic species of the metal to be more toxic in one water than the other, or causes a shift in the ratios of various toxic species, we can define

$$H = \frac{T_S + \Delta T_S}{T_L + \Delta T_L} .$$

Thus H is a multiplier that accounts for a proportional increase or decrease in the toxicity of the toxic forms in site water as compared to their toxicities in laboratory dilution water. Therefore, the general WER equation is:

$$WER = \frac{R_S + N_S + \Delta N_S + H(T_L + \Delta T_L)}{R_L + N_L + \Delta N_L + (T_L + \Delta T_L)} .$$

Several things are obvious from this equation:
1. A WER should not be thought of as a simple ratio such as H. H is the ratio of the toxicities of the toxic species of the metal, whereas the WER is the ratio of the sum of the toxic and the nontoxic species of the metal. Only under a very specific set of conditions will $WER = H$. If these conditions are satisfied and if, in addition, $H = 1$, then $WER = 1$. Although it might seem that all of these conditions will rarely be satisfied, it is not all that rare to find that an experimentally determined WER is close to 1.
2. When the concentration of metal in laboratory dilution water is negligible, $R_L = N_L = T_L = 0$ and

$$WER = \frac{R_S + N_S + \Delta N_S + H(\Delta T_L)}{\Delta N_L + \Delta T_L} .$$

Even though laboratory dilution water is low in TOC and TSS, when metals are added to laboratory dilution water in toxicity tests, ions such as hydroxide, carbonate, and chloride react with some metals to form some particulate species and some dissolved species, both of which might be toxic or nontoxic. The metal species that are nontoxic contribute to ΔN_L, whereas those that are toxic contribute to ΔT_L. Hydroxide, carbonate, chloride, TOC, and TSS can increase ΔN_S. Anything that causes ΔN_S to differ from ΔN_L will cause the WER to differ from 1.

3. Refractory metal and nontoxic labile metal in the site water above that in the laboratory dilution water will increase the WER. Therefore, if the WER is determined in downstream water, rather than in upstream water, the WER will be increased by refractory metal and nontoxic labile metal in the effluent.

Thus there are three major reasons why WERs might be larger or smaller than 1:

a. The toxic species of the metal might be more toxic in one water than in the other, i.e., $H \neq 1$.
b. ΔN might be higher in one water than in the other.
c. R and/or N might be higher in one water than in the other.

The last reason might have great practical importance in some situations. When a WER is determined in downstream water, if most of the metal in the effluent is nontoxic, the WER and the endpoint in site water will correlate with the concentration of metal in the site water. In addition, they will depend on the concentration of metal in the effluent and the concentration of effluent in the site water. This correlation will be best for refractory metal because its toxicity cannot be affected by water quality characteristics; even if the effluent and upstream water are quite different so that the water quality characteristics of the site water depend on the percent effluent, the toxicity of the refractory metal will remain constant at zero and the portion of the WER that is due to refractory metal will be additive.

The Dependence of WERs on the Sensitivity of Toxicity Tests

It would be desirable if the magnitude of the WER for a site water were independent of the toxicity test used in the determination of the WER, so that any convenient toxicity test could be used. It can be seen from the general WER equation that the WER will be independent of the toxicity test only if:

$$WER = \frac{H(T_L + \Delta T_L)}{(T_L + \Delta T_L)} = H \, ,$$

which would require that $R_S = N_S = \Delta N_S = R_L = N_L = \Delta N_L = 0$. (It would be easy to assume that $T_L = 0$, but it can be misleading in some situations to make more simplifications than are necessary.)

This is the simplistic concept of a WER that would be advantageous if it were true, but which is not likely to be true very often. Any situation in which one or more of the terms is greater than zero can cause the WER to depend on the sensitivity of the toxicity test, although the difference in the WERs might be small.

Two situations that might be common can illustrate how the WER can depend on the sensitivity of the toxicity test. For these illustrations, there is no advantage to assuming that $H = 1$, so H will be retained for generality.

1. The simplest situation is when $R_S > 0$, i.e., when a substantial concentration of refractory metal occurs in the site water. If, for simplification, it is assumed that $N_S = \Delta N_S = R_L = N_L = \Delta N_L = 0$, then:

$$WER = \frac{R_S + H(T_L + \Delta T_L)}{(T_L + \Delta T_L)} = \frac{R_S}{(T_L + \Delta T_L)} + H \ .$$

   The quantity $T_L + \Delta T_L$ obviously changes as the sensitivity of the toxicity test changes. When $R_S = 0$, then $WER = H$ and the WER is independent of the sensitivity of the toxicity test. When $R_S > 0$, then the WER will decrease as the sensitivity of the test decreases because $T_L + \Delta T_L$ will increase.

2. More complicated situations occur when $(N_S + \Delta N_S) > 0$. If, for simplification, it is assumed that $R_S = R_L = N_L = \Delta N_L = 0$, then:

$$WER = \frac{(N_S + \Delta N_S) + H(T_L + \Delta T_L)}{(T_L + \Delta T_L)} = \frac{(N_S + \Delta N_S)}{(T_L + \Delta T_L)} + H \ .$$

   a. If $(N_S + \Delta N_S) > 0$ because the site water contains a substantial concentration of a complexing agent that has an affinity for the metal and if complexation converts toxic metal into nontoxic metal, the complexation reaction will control the toxicity of the solution (Allen 1993). A complexation curve can be graphed in several ways, but the S-shaped curve presented in Figure D5 is most convenient here. The vertical axis is "% uncomplexed", which is assumed to correlate with "% toxic". The "% complexed" is then the "% nontoxic". The ratio of nontoxic metal to toxic metal is:

$$\frac{\%nontoxic}{\%toxic} = \frac{\%complexed}{\%uncomplexed} = V \ .$$

   For the complexed nontoxic metal:

$$V = \frac{concentration\ of\ nontoxic\ metal}{concentration\ of\ toxic\ metal} \ .$$

In the site water, the concentration of complexed nontoxic metal is $(N_S + \Delta N_S)$ and the concentration of toxic metal is $(T_S + \Delta T_S)$, so that:

$$V_S = \frac{(N_S + \Delta N_S)}{(T_S + \Delta T_S)} = \frac{(N_S + \Delta N_S)}{H(T_L + \Delta T_L)} \ .$$

and

$$WER = \frac{V_S H(T_L + \Delta T_L) + H(T_L + \Delta T_L)}{(T_L + \Delta T_L)} = V_S H + H = H(V_S + 1) \ .$$

If the WER is determined using a sensitive toxicity test so that the % uncomplexed (i.e., the % toxic) is 10 %, then $V_S = (90\ \%)/(10\ \%) = 9$, whereas if a less sensitive test is used so that the % uncomplexed is 50 %, then $V_S = (50\ \%)/(50\ \%) = 1$. Therefore, if a portion of the WER is due to a complexing agent in the site water, the magnitude of the WER can decrease as the sensitivity of the toxicity test decreases because the % uncomplexed will decrease. In these situations, the largest WER will be obtained with the most sensitive toxicity test; progressively smaller WERs will be obtained with less sensitive toxicity tests. The magnitude of a WER will depend not only on the sensitivity of the toxicity test but also on the concentration of the complexing agent and on its binding constant (complexation constant, stability constant). In addition, the binding constants of most complexing agents depend on pH.

If the laboratory dilution water contains a low concentration of a complexing agent,

$$V_L = \frac{N_L + \Delta N_L}{T_L + \Delta T_L}$$

and

$$WER = \frac{V_S H(T_L + \Delta T_L) + H(T_L + \Delta T_L)}{V_L(T_L + \Delta T_L) + (T_L + \Delta T_L)} = \frac{V_S H + H}{V_L + 1} = \frac{H(V_S + 1)}{V_L + 1} \ .$$

The binding constant of the complexing agent in the laboratory dilution water is probably different from that of the complexing agent in the site water. Although changing from a more sensitive test to a less sensitive test will decrease both V_S and V_L, the amount of effect is not likely to be proportional.

If the change from a more sensitive test to a less sensitive test were to decrease V_L proportionately more than V_S, the change could result in a larger WER, rather than a smaller WER, as resulted in the case above when it was assumed that the laboratory dilution water did not contain any complexing agent. This is probably most likely to occur if $H = 1$ and if $V_S < V_L$, which would mean that $WER < 1$. Although this is likely to be a rare situation, it does demonstrate again the importance of determining WERs using toxicity tests that have endpoints in laboratory dilution water that are close to the CMC or CCC to which the WER is to be applied.

b. If $(N_S + \Delta N_S) > 0$ because the site water contains a substantial concentration of an ion that will precipitate the metal of concern and if precipitation converts toxic metal into nontoxic metal, the precipitation reaction will control the toxicity of the solution. The "precipitation curve" given in Figure D6 is analogous to the "complexation curve" given in Figure D5; in the precipitation curve, the vertical axis is "% dissolved", which is assumed to correlate with "% toxic". If the endpoint for a toxicity test is below the solubility limit of the precipitate, $(N_S + \Delta N_S) = 0$, whereas if the endpoint for a toxicity test is above the solubility limit, $(N_S + \Delta N_S) > 0$. If WERs are determined with a series of toxicity tests that have increasing endpoints that are above the solubility limit, the WER will reach a maximum value and then decrease. The magnitude of the WER will depend not only on the sensitivity of the toxicity test but also on the concentration of the precipitating agent, the solubility limit, and the solubility of the precipitate.

Thus, depending on the composition of the site water, a WER obtained with an insensitive test might be larger, smaller, or similar to a WER obtained with a sensitive test. Because of the range of possibilities that exist, the best toxicity test to use in the experimental determination of a WER is one whose endpoint in laboratory dilution water is close to the CMC or CCC that is to be adjusted. This is the rationale that was used in the selection of the toxicity tests that are suggested in Appendix I.

The available data indicate that a less sensitive toxicity test usually gives a smaller WER than a more sensitive test (Hansen 1993a). Thus, use of toxicity tests whose endpoints are higher than the CMC or CCC probably will not result in underprotection; in contrast, use of tests whose endpoints are substantially below the CMC or CCC might result in underprotection.

The factors that cause R_S and $(N_S + \Delta N_S)$ to be greater than zero are all external to the test organisms; they are chemical effects that affect the metal in the water. The magnitude of the WER is therefore expected to depend on the toxicity test used only in regard to the sensitivity of the test. If the endpoints for two different tests occur at the same concentration of the metal, the magnitude of the WERs obtained with the two tests should be the same; they should not depend on (a) the duration of the test, (b) whether the endpoint is based on a lethal or sublethal effect, or (c) whether the species is a vertebrate or an invertebrate.

Another interesting consequence of the chemistry of complexation is that the % uncomplexed will increase if the solution is diluted (Allen and Hansen 1993). The concentration of total metal will decrease with dilution but the % uncomplexed will increase. The increase will not offset the decrease and so the concentration of uncomplexed metal will decrease. Thus the portion of a WER that is due to complexation will not be strictly additive (see Appendix G), but the amount of nonadditivity might be difficult to detect in toxicity studies of additivity. A similar effect of dilution will occur for precipitation.

The illustrations presented above were simplified to make it easier to understand the kinds of effects that can occur. The illustrations are qualitatively valid and demonstrate the direction of the effects, but real-world situations will probably be so much more complicated that the various effects cannot be dealt with separately.

Other Properties of WERs

1. Because of the variety of factors that can affect WERs, no rationale exists at present for extrapolating WERs from one metal to another, from one effluent to another, or from one surface water to another. Thus WERs should be individually determined for each metal at each site.

2. The most important information that the determination of a WER provides is whether simulated and/or actual downstream water adversely affects test organisms that are sensitive to the metal. A WER cannot indicate how much metal needs to be removed from or how much metal can be added to an effluent.
   a. If the site water already contains sufficient metal that it is toxic to the test organisms, a WER cannot be determined with a sensitive test and so an insensitive test will have to be used. Even if a WER could be determined with a sensitive test, the WER cannot indicate how much metal has to be removed. For example, if a WER indicated that there was 20 percent too much metal in an effluent, a 30 percent reduction by the discharger would not reduce toxicity if only nontoxic metal was removed. The next WER determination would show that the effluent still contained too much metal. Removing metal is useful only if the metal removed is toxic metal. Reducing the total recoverable concentration does not necessarily reduce toxicity.

b. If the simulated or actual downstream water is not toxic, a WER can be determined and used to calculate how much additional metal the effluent could contain and still be acceptable. Because an unlimited amount of refractory metal can be added to the effluent without affecting the organisms, what the WER actually determines is how much additional toxic metal can be added to the effluent.

3. The effluent component of nearly all WERs is likely to be due mostly to either (a) a reduction in toxicity of the metal by TSS or TOC, or (b) the presence of refractory metal. For both of these, if the percentage of effluent in the downstream water decreases, the magnitude of the WER will usually decrease. If the water quality characteristics of the effluent and the upstream water are quite different, it is possible that the interaction will not be additive; this can affect the portion of the WER that is due to reduced toxicity caused by sorption and/or binding, but it cannot affect the portion of the WER that is due to refractory metal.

4. Test organisms are fed during some toxicity tests, but not during others; it is not clear whether a WER determined in a fed test will differ from a WER determined in an unfed test. Whether there is a difference is likely to depend on the metal, the type and amount of food, and whether a total recoverable or dissolved WER is determined. This can be evaluated by determining two WERs using a test in which the organisms usually are not fed - one WER with no food added to the tests and one with food added to the tests. Any effect of food is probably due to an increase in TOC and/or TSS. If food increases the concentration of nontoxic metal in both the laboratory dilution water and the site water, the food will probably decrease the WER. Because complexes of metals are usually soluble, complexation is likely to lower both total recoverable and dissolved WERs; sorption to solids will probably reduce only total recoverable WERs. The food might also affect the acute-chronic ratio. Any feeding during a test should be limited to the minimum necessary.

Ranges of Actual Measured WERs

The acceptable WERs found by Brungs et al. (1992) were total recoverable WERs that were determined in relatively clean fresh water. These WERs ranged from about 1 to 15 for both copper and cadmium, whereas they ranged from about 0.7 to 3 for zinc. The few WERs that were available for chromium, lead, and nickel ranged from about 1 to 6. Both the total recoverable and dissolved WERs for copper in New York harbor range from about 0.4 to 4 with most of the WERs being between 1 and 2 (Hansen 1993b).

Figure D2: An Example of the Empirical Extrapolation Process

Assume the following hypothetical effluent and upstream water:

Effluent:

T_E:	100 ug/L	
D_E:	10 ug/L	(10 % dissolved)
Q_E:	24 cfs	

Upstream water:

T_U:	40 ug/L	
D_U:	38 ug/L	(95 % dissolved)
Q_U:	48 cfs	

Downstream water:

T_D:	60 ug/L	
D_D:	36 ug/L	(60 % dissolved)
Q_D:	72 cfs	

where:

T = concentration of total recoverable metal.
D = concentration of dissolved metal.
Q = flow.

The subscripts E, U, and D signify effluent, upstream water, and downstream water, respectively.

By conservation of flow: $Q_D = Q_E + Q_U$.

By conservation of total recoverable metal: $T_D Q_D = T_E Q_E + T_U Q_U$.

If P = the percent of the total recoverable metal in the effluent that becomes dissolved in the downstream water,

$$P = \frac{100\,(D_D Q_D - D_U Q_U)}{T_E Q_E} \quad .$$

For the data given above, the percent of the total recoverable metal in the effluent that becomes dissolved in the downstream water is:

$$P = \frac{100[(36\ ug/L)(72\ cfs) - (38\ ug/L)(48\ cfs)]}{(100\ ug/L)(24\ cfs)} = 32\ \% \ ,$$

which is greater than the 10 % dissolved in the effluent and less than the 60 % dissolved in the downstream water.

Figure D3: The Internal Consistency of the Two Approaches

The internal consistency of the total recoverable and dissolved approaches can be illustrated by considering the use of WERs to interpret the total recoverable and dissolved concentrations of a metal in a site water. For this hypothetical example, it will be assumed that the national CCCs for the metal are:

200 ug/L as total recoverable metal.
160 ug/L as dissolved metal.

It will also be assumed that the concentrations of the metal in the site water are:

300 ug/L as total recoverable metal.
120 ug/L as dissolved metal.

The total recoverable concentration in the site water exceeds the national CCC, but the dissolved concentration does not.

The following results might be obtained if WERs are determined:

<u>In Laboratory Dilution Water</u>

Total recoverable LC50 = 400 ug/L.
% of the total recoverable metal that is dissolved = 80.
(This is based on the ratio of the national CCCs, which were determined in laboratory dilution water.)
Dissolved LC50 = 320 ug/L.

<u>In Site Water</u>

Total recoverable LC50 = 620 ug/L.
% of the total recoverable metal that is dissolved = 40.
(This is based on the data given above for site water).
Dissolved LC50 = 248 ug/L.

<u>WERs</u>

Total recoverable WER = (620 ug/L)/(400 ug/L) = 1.55
Dissolved WER = (248 ug/L)/(320 ug/L) = 0.775

<u>Checking the Calculations</u>

$$\frac{\textit{Total recoverable WER}}{\textit{Dissolved WER}} = \frac{1.55}{0.775} = \frac{\textit{lab water \% dissolved}}{\textit{site water \% dissolved}} = \frac{80}{40} = 2$$

<u>Site-specific CCCs (ssCCCs)</u>

Total recoverable ssCCC = (200 ug/L)(1.55) = 310 ug/L.
Dissolved ssCCC = (160 ug/L)(0.775) = 124 ug/L.

Both concentrations in site water are below the respective ssCCCs.

In contrast, the following results might have been obtained when the WERs were determined:

<u>In Laboratory Dilution Water</u>

Total recoverable LC50 = 400 ug/L.

% of the total recoverable metal that is dissolved = 80.

Dissolved LC50 = 320 ug/L.

<u>In Site Water</u>

Total recoverable LC50 = 580 ug/L.

% of the total recoverable metal that is dissolved = 40.

Dissolved LC50 = 232 ug/L.

<u>WERs</u>

Total recoverable WER = (580 ug/L)/(400 ug/L) = 1.45

Dissolved WER = (232 ug/L)/(320 ug/L) = 0.725

<u>Checking the Calculations</u>

$$\frac{\textit{Total recoverable WER}}{\textit{Dissolved WER}} = \frac{1.45}{0.725} = \frac{\textit{lab water \% dissolved}}{\textit{site water \% dissolved}} = \frac{80}{40} = 2$$

<u>Site-specific CCCs (ssCCCs)</u>

Total recoverable ssCCC = (200 ug/L)(1.45) = 290 ug/L.

Dissolved ssCCC = (160 ug/L)(0.725) = 116 ug/L.

In this case, both concentrations in site water are above the respective ssCCCs.

In each case, both approaches resulted in the same conclusion concerning whether the concentration in site water exceeds the site-specific criterion.

The two key assumptions are:

1. The ratio of total recoverable metal to dissolved metal in laboratory dilution water when the WERs are determined equals the ratio of the national CCCs.
2. The ratio of total recoverable metal to dissolved metal in site water when the WERs are determined equals the ratio of the concentrations reported in the site water.

Differences in the ratios that are outside the range of experimental variation will cause problems for the derivation of site-specific criteria and, therefore, with the internal consistency of the two approaches.

Figure D4: The Application of the Two Approaches

Hypothetical upstream water and effluent will be used to demonstrate the equivalence of the total recoverable and dissolved approaches. The upstream water and the effluent will be assumed to have specific properties in order to allow calculation of the properties of the downstream water, which will be assumed to be a 1:1 mixture of the upstream water and effluent. It will also be assumed that the ratios of the forms of the metal in the upstream water and in the effluent do not change when the total recoverable concentration changes.

<u>Upstream water</u> (Flow = 3 cfs)

Total recoverable:	400 ug/L	
Refractory particulate:	200 ug/L	
Toxic dissolved:	200 ug/L	(50 % dissolved)

<u>Effluent</u> (Flow = 3 cfs)

Total recoverable:	440 ug/L	
Refractory particulate:	396 ug/L	
Labile nontoxic particulate:	44 ug/L	
Toxic dissolved:	0 ug/L	(0 % dissolved)

(The labile nontoxic particulate, which is 10 % of the total recoverable in the effluent, becomes toxic dissolved in the downstream water.)

<u>Downstream water</u> (Flow = 6 cfs)

Total recoverable:	420 ug/L	
Refractory particulate:	298 ug/L	
Toxic dissolved:	122 ug/L	(29 % dissolved)

The values for the downstream water are calculated from the values for the upstream water and the effluent:

Total recoverable:	[3(400) + 3(440)]/6	= 420 ug/L
Dissolved:	[3(200) + 3(44+0)]/6	= 122 ug/L
Refractory particulate:	[3(200) + 3(396)]/6	= 298 ug/L

<u>Assumed National CCC (nCCC)</u>

Total recoverable = 300 ug/L
Dissolved = 240 ug/L

Upstream site-specific CCC (ussCCC)

Assume: Dissolved cccWER = 1.2
Dissolved ussCCC = (1.2)(240 ug/L) = 288 ug/L
By calculation: TR ussCCC = (288 ug/L)/(0.5) = 576 ug/L
Total recoverable cccWER = (576 ug/L)/(300 ug/L) = 1.92

	nCCC	cccWER	ussCCC	Conc.
Total recoverable:	300 ug/L	1.92	576 ug/L	400 ug/L
Dissolved:	240 ug/L	1.2	288 ug/L	200 ug/L
% dissolved	80 %	----	50 %	50 %

Neither concentration exceeds its respective ussCCC.

$$\frac{\textit{Total recoverable WER}}{\textit{Dissolved WER}} = \frac{1.92}{1.2} = \frac{\textit{lab water \% dissolved}}{\textit{site water \% dissolved}} = \frac{80}{50} = 1.6$$

Downstream site-specific CCC (dssCCC)

Assume: Dissolved cccWER = 1.8
Dissolved dssCCC = (1.8)(240 ug/L) = 432 ug/L
By calculation: TR dssCCC =
{(432 ug/L-[(200 ug/L)/2])/0.1}+{(400 ug/L)/2} = 3520 ug/L
This calculation determines the amount of dissolved metal contributed by the effluent, accounts for the fact that ten percent of the total recoverable metal in the effluent becomes dissolved, and adds the total recoverable metal contributed by the upstream flow.
Total recoverable cccWER = (3520 ug/L)/(300 ug/L) = 11.73

	nCCC	cccWER	dssCCC	Conc.
Total recoverable:	300 ug/L	11.73	3520 ug/L	420 ug/L
Dissolved:	240 ug/L	1.80	432 ug/L	122 ug/L
% dissolved	80 %	----	12.27 %	29 %

Neither concentration exceeds its respective dssCCC.

$$\frac{\textit{Total recoverable WER}}{\textit{Dissolved WER}} = \frac{11.73}{1.80} = \frac{\textit{lab water \% dissolved}}{\textit{site water \% dissolved}} = \frac{80}{12.27} = 6.52$$

Calculating the Maximum Acceptable Concentration in the Effluent

Because neither the total recoverable concentration nor the dissolved concentration in the downstream water exceeds its respective site-specific CCC, the concentration of metal in the effluent could be increased. Under the assumption that the ratios of the two forms of the metal in the effluent do not change when the total recoverable concentration changes, the maximum acceptable concentration of total recoverable metal in the effluent can be calculated as follows:

Starting with the total recoverable dssCCC of 3520 ug/L

$$\frac{(6\ cfs)(3520\ ug/L) - (3\ cfs)(400\ ug/L)}{3\ cfs} = 6640\ ug/L$$

Starting with the dissolved dssCCC of 432 ug/L

$$\frac{(6\ cfs)(432\ ug/L) - (3\ cfs)(400\ ug/L)(0.5)}{(3\ cfs)(0.10)} = 6640\ ug/L$$

Checking the Calculations

Total recoverable:

$$\frac{(3\ cfs)(6640\ ug/L) + (3\ cfs)(400\ ug/L)}{6\ cfs} = 3520\ ug/L\ .$$

Dissolved:

$$\frac{(3\ cfs)(6640\ ug/L)(0.10) + (3\ cfs)(400\ ug/L)(0.50)}{6\ cfs} = 432\ ug/L\ .$$

The value of 0.10 is used because this is the percent of the total recoverable metal in the effluent that becomes dissolved in the downstream water.

The values of 3520 ug/L and 432 ug/L equal the downstream site-specific CCCs derived above.

Another Way to Calculate the Maximum Acceptable Concentration

The maximum acceptable concentration of total recoverable metal in the effluent can also be calculated from the dissolved dssCCC of 432 ug/L using a partition coefficient to convert from the dissolved dssCCC of 432 ug/L to the total recoverable dssCCC of 3520 ug/L:

$$\frac{[6\ cfs]\left[\frac{432\ ug/L}{0.1227} - (3\ cfs)(400\ ug/L)\right]}{3\ cfs} = 6640\ ug/L\ .$$

Note that the value used for the partition coefficient in this calculation is 0.1227 (the one that applies to the downstream water when the total recoverable concentration of metal in the effluent is 6640 ug/L), not 0.29 (the one that applies when the concentration of metal in the effluent is only 420 ug/L). The three ways of calculating the maximum acceptable concentration give the same result if each is used correctly.

Figure D5: A Generalized Complexation Curve

The curve is for a constant concentration of the complexing ligand and an increasing concentration of the metal.

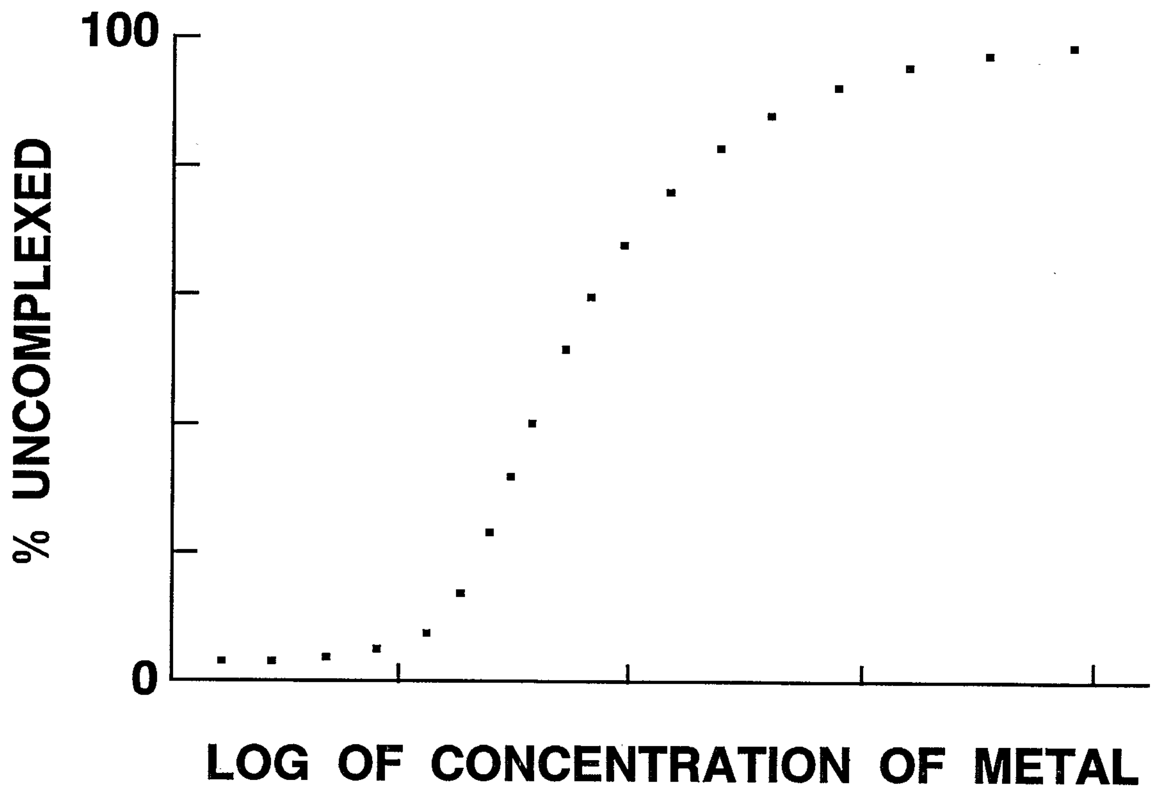
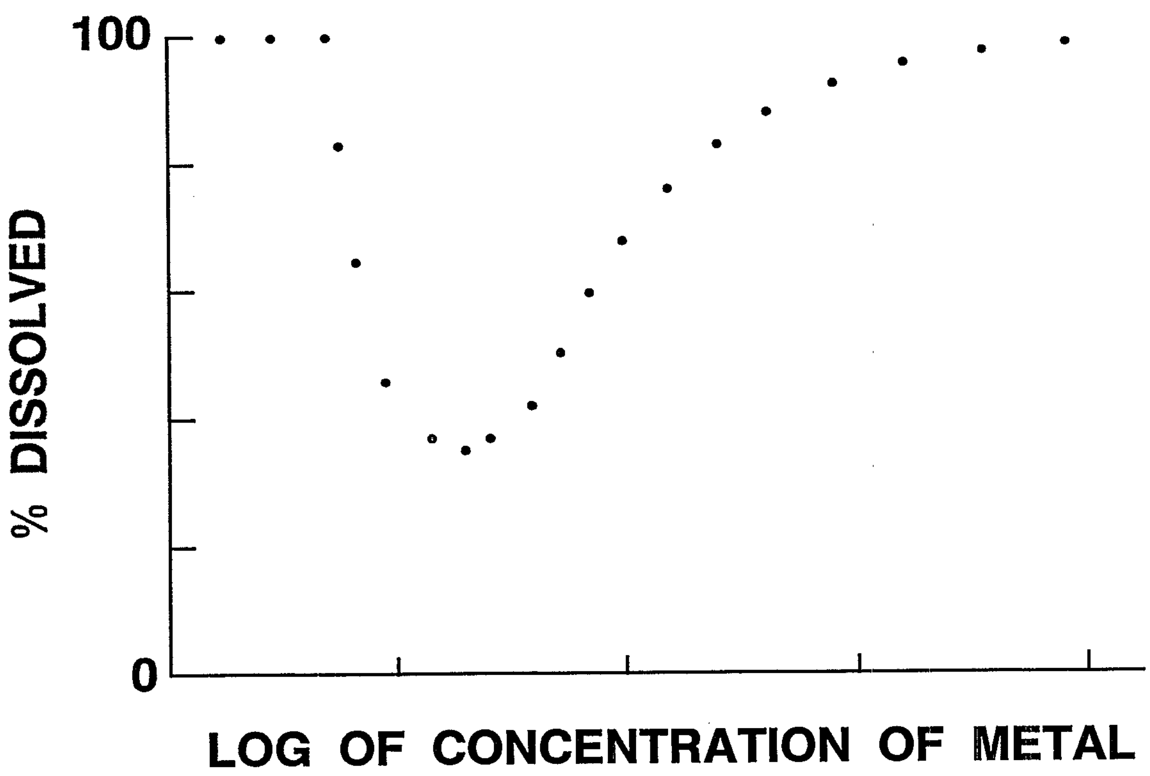


Figure D6: A Generalized Precipitation Curve

The curve is for a constant concentration of the precipitating ligand and an increasing concentration of the metal.



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Appendix E: U.S. EPA Aquatic Life Criteria Documents for Metals

Metal	EPA Number	NTIS Number
Aluminum	EPA 440/5-86-008	PB88-245998
Antimony	EPA 440/5-80-020	PB81-117319
Arsenic	EPA 440/5-84-033	PB85-227445
Beryllium	EPA 440/5-80-024	PB81-117350
Cadmium	EPA 440/5-84-032	PB85-227031
Chromium	EPA 440/5-84-029	PB85-227478
Copper	EPA 440/5-84-031	PB85-227023
Lead	EPA 440/5-84-027	PB85-227437
Mercury	EPA 440/5-84-026	PB85-227452
Nickel	EPA 440/5-86-004	PB87-105359
Selenium	EPA 440/5-87-006	PB88-142237
Silver	EPA 440/5-80-071	PB81-117822
Thallium	EPA 440/5-80-074	PB81-117848
Zinc	EPA 440/5-87-003	PB87-153581

All are available from:

National Technical Information Service (NTIS)
5285 Port Royal Road
Springfield, VA 22161
TEL: 703-487-4650

Appendix F: Considerations Concerning Multiple-Metal, Multiple-Discharge, and Special Flowing-Water Situations

Multiple-Metal Situations

Both Method 1 and Method 2 work well in multiple-metal situations, although the amount of testing required increases as the number of metals increases. The major problem is the same for both methods: even when addition of two or more metals individually is acceptable, simultaneous addition of the two or more metals, each at its respective maximum acceptable concentration, might be unacceptable for at least two reasons:

1. Additivity or synergism might occur between metals.
2. More than one of the metals might be detoxified by the same complexing agent in the site water. When WERs are determined individually, each metal can utilize all of the complexing capacity; when the metals are added together, however, they cannot simultaneously utilize all of the complexing capacity.

Thus a discharger might feel that it is cost-effective to try to justify the lowest site-specific criterion that is acceptable to the discharger rather than trying to justify the highest site-specific criterion that the appropriate regulatory authority might approve.

There are two options for dealing with the possibility of additivity and synergism between metals:

a. WERs could be developed using a mixture of the metals but it might be necessary to use several primary toxicity tests depending on the specific metals that are of interest. Also, it might not be clear what ratio of the metals should be used in the mixture.

b. If a WER is determined for each metal individually, one or more additional toxicity tests **must** be conducted at the end to show that the combination of all metals at their proposed new site-specific criteria is acceptable. Acceptability **must** be demonstrated with each toxicity test that was used as a primary toxicity test in the determination of the WERs for the individual metals. Thus if a different primary test was used for each metal, the number of acceptability tests needed would equal the number of metals. It is possible that a toxicity test used as the primary test for one metal might be more sensitive than the CMC (or CCC) for another metal and thus might not be usable in the combination test unless antagonism occurs. When a primary test cannot be used, an acceptable alternative test **must** be used.

The second option is preferred because it is more definitive; it provides data for each metal individually and for the mixture. The first option leaves the possibility that one of the metals is antagonistic towards another so that the toxicity of the mixture would increase if the metal causing the antagonism were not present.

Multiple-Discharge Situations

Because the National Toxics Rule (NTR) incorporated WERs into the aquatic life criteria for some metals, it might be envisioned that more than one criterion could apply to a metal at a site if different investigators obtained different WERs for the same metal at the site. In jurisdictions subject to the NTR, as well as in all other jurisdictions, EPA intends that there should be no more than one criterion for a pollutant at a point in a body of water. Thus whenever a site-specific criterion is to be derived using a WER at a site at which more than one discharger has permit limits for the same metal, it is important that all dischargers work together with the appropriate regulatory authority to develop a workplan that is designed to derive a site-specific criterion that adequately protects the entire site.

Method 2 is ideally suited for taking into account more than one discharger.

Method 1 is straightforward if the dischargers are sufficiently far downstream of each other that the stream can be divided into a separate site for each discharger. Method 1 can also be fairly straightforward if the WERs are additive, but it will be complex if the WERs are not additive. Deciding whether to use a simulated downstream water or an actual downstream water can be difficult in a flowing-water multiple-discharge situation. Use of actual downstream water can be complicated by the existence of multiple mixing zones and plumes and by the possibility of varying discharge schedules; these same problems exist, however, if effluents from two or more discharges are used to prepare simulated downstream water. Dealing with a multiple-discharge situation is much easier if the WERs are additive, and use of simulated downstream water is the best way to determine whether the WERs are additive. Taking into account all effluents will take into account synergism, antagonism, and additivity. If one of the discharges stops or is modified substantially, however, it will usually be necessary to determine a new WER, except possibly if the metal being discharged is refractory. Situations concerning intermittent and batch discharges need to be handled on a case-by-case basis.

Special Flowing-Water Situations

Method 1 is intended to apply not only to ordinary rivers and streams but also to streams that some people might consider "special", such as streams whose design flows are zero and streams that some state and/or federal agencies might refer to as "effluent-dependent", "habitat-creating", "effluent-dominated", etc. (Due to differences between agencies, some streams whose design flows are zero are not considered "effluent-dependent", etc., and some "effluent-dependent" streams have design flows that are greater than zero.) The application of Method 1 to these kinds of streams has the following implications:

1. If the design flow is zero, at least some WERs ought to be determined in 100% effluent.
2. If thunderstorms, etc., occasionally dilute the effluent substantially, at least one WER should be determined in diluted effluent to assess whether dilution by rainwater might result in underprotection by decreasing the WER faster than it decreases the concentration of the metal. This might occur, for example, if rainfall reduces hardness, alkalinity, and pH substantially. This might not be a concern if the WER demonstrates a substantial margin of safety.
3. If the site-specific criterion is substantially higher than the national criterion, there should be increased concern about the fate of the metal that has reduced or no toxicity. Even if the WER demonstrates a substantial margin of safety (e.g., if the site-specific criterion is three times the national criterion, but the experimentally determined WER is 11), it might be desirable to study the fate of the metal.
4. If the stream merges with another body of water and a site-specific criterion is desired for the merged waters, another WER needs to be determined for the mixture of the waters.
5. Whether WET testing is required is not a WER issue, although WET testing might be a condition for determining and/or using a WER.
6. A concern about what species should be present and/or protected in a stream is a beneficial-use issue, not a WER issue, although resolution of this issue might affect what species should be used if a WER is determined. (If the Recalculation Procedure is used, determining what species should be present and/or protected is obviously important.)
7. Human health and wildlife criteria and other issues might restrict an effluent more than an aquatic life criterion.

Although there are no scientific reasons why "effluent-dependent", etc., streams and streams whose design flows are zero should be subject to different guidance than other streams, a regulatory decision (for example, see 40 CFR 131) might require or allow some or all such streams to be subject to different guidance. For example, it might be decided on the basis of a use attainability analysis that one or more constructed streams do not have to comply with usual aquatic life criteria because it is decided that the water quality in such streams does not need to protect sensitive aquatic species. Such a decision might eliminate any further concern for site-specific aquatic life criteria and/or for WET testing for such streams. The water quality might be unacceptable for other reasons, however.

In addition to its use with rivers and streams, Method 1 is also appropriate for determining cmcWERs that are applicable to near-field effects of discharges into large bodies of fresh or salt water, such as an ocean or a large lake, reservoir, or estuary:

a. The near-field effects of a pipe that extends far into a large body of fresh or salt water that has a current, such as an ocean, can probably best be treated the same as a single discharge into a flowing stream. For example, if a mixing zone is defined, the concentration of effluent at the edge of the mixing zone might be used to define how to prepare a simulated site water. A dye dispersion study (Kilpatrick 1992) might be useful, but a dilution model (U.S. EPA 1993) is likely to be a more cost-effective way of obtaining information concerning the amount of dilution at the edge of the mixing zone.

b. The near-field effects of a single discharge that is near a shore of a large body of fresh or salt water can also probably best be treated the same as a single discharge into a flowing stream, especially if there is a definite plume and a defined mixing zone. The potential point of impact of near-field effects will often be an embayment, bayou, or estuary that is a nursery for fish and invertebrates and/or contains commercially important shellfish beds. Because of their importance, these areas should receive special consideration in the determination and use of a WER, taking into account sources of water and discharges, mixing patterns, and currents (and tides in coastal areas). The current and flushing patterns in estuaries can result in increased pollutant concentrations in confined embayments and at the terminal up-gradient portion of the estuary due to poor tidal flushing and exchange. Dye dispersion studies (Kilpatrick 1992) can be used to determine the spatial concentration of the effluent in the receiving water, but dilution models (U.S. EPA 1993) might not be sufficiently accurate to be useful. Dye studies of discharges in near-shore tidal areas are especially complex. Dye injection into the discharge should occur over at least one, and preferably two or three, complete tidal cycles; subsequent dispersion patterns should be monitored in the ambient water on consecutive tidal cycles using an intensive sampling regime over time, location, and depth. Information concerning dispersion and the community at risk can be used to define the appropriate mixing zone(s), which might be used to define how to prepare simulated site water.

References

Kilpatrick, F.A. 1992. Simulation of Soluble Waste Transport and Buildup in Surface Waters Using Tracers. Open-File Report 92-457. U.S. Geological Survey, Books and Open-File Reports, Box 25425, Federal Center, Denver, CO 80225.

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Appendix G: Additivity and the Two Components of a WER Determined Using Downstream Water

The Concept of Additivity of WERs

In theory, whenever samples of effluent and upstream water are taken, determination of a WER in 100 % effluent would quantify the effluent WER (eWER) and determination of a WER in 100 % upstream water would quantify the upstream WER (uWER); determination of WERs in known mixtures of the two samples would demonstrate whether the eWER and the uWER are additive. For example, if eWER = 40, uWER = 5, and the two WERs are additive, a mixture of 20 % effluent and 80 % upstream water would give a WER of 12, except possibly for experimental variation, because:

$$\frac{20(eWER) + 80(uWER)}{100} = \frac{20(40) + 80(5)}{100} = \frac{800 + 400}{100} = \frac{1200}{100} = 12 .$$

Strict additivity of an eWER and an uWER will probably be rare because one or both WERs will probably consist of a portion that is additive and a portion that is not. The portions of the eWER and uWER that are due to refractory metal will be strictly additive, because a change in water quality will not make the metal more or less toxic. In contrast, metal that is nontoxic because it is complexed by a complexing agent such as EDTA will not be strictly additive because the % uncomplexed will decrease as the solution is diluted; the amount of change in the % uncomplexed will usually be small and will depend on the concentration and the binding constant of the complexing agent (see Appendix D). Whether the nonrefractory portions of the uWER and eWER are additive will probably also depend on the differences between the water quality characteristics of the effluent and the upstream water, because these will determine the water quality characteristics of the downstream water. If, for example, 85 % of the eWER and 30 % of the uWER are due to refractory metal, the WER obtained in the mixture of 20 % effluent and 80 % upstream water could range from 8 to 12. The WER of 8 would be obtained if the only portions of the eWER and uWER that are additive are those due to refractory metal, because:

$$\frac{20(0.85)(eWER) + 80(0.30)(uWER)}{100} = \frac{20(0.85)(40) + 80(0.30)(5)}{100} = 8 .$$

The WER could be as high as 12 depending on the percentages of the other portions of the WERs that are also additive. Even if the eWER and uWER are not strictly additive, the concept of additivity of WERs can be useful insofar as the eWER and uWER are partially additive, i.e., insofar as a portion of at least one of the WERs is additive. In the example given above, the WER determined using downstream water that consisted of 20 % effluent and 80 % upstream water would be 12 if the eWER and uWER were strictly additive; the downstream WER would be less than 12 if the eWER and uWER were partially additive.

The Importance of Additivity

The major advantage of additivity of WERs can be demonstrated using the effluent and upstream water that were used above. To simplify this illustration, the acute-chronic ratio will be assumed to be large, and the eWER of 40 and the uWER of 5 will be assumed to be cccWERs that will be assumed to be due to refractory metal and will therefore be strictly additive. In addition, the complete-mix downstream water at design-flow conditions will be assumed to be 20 % effluent and 80 % upstream water, so that the downstream WER will be 12 as calculated above for strict additivity.

Because the eWER and the uWER are cccWERs and are strictly additive, this metal will cause neither acute nor chronic toxicity in downstream water if (a) the concentration of metal in the effluent is less than 40 times the CCC and (b) the concentration of metal in the upstream water is less than 5 times the CCC. As the effluent is diluted by mixing with upstream water, both the eWER and the concentration of metal will be diluted simultaneously; proportional dilution of the metal and the eWER will prevent the metal from causing acute or chronic toxicity at any dilution. When the upstream flow equals the design flow, the WER in the plume will decrease from 40 at the end of the pipe to 12 at complete mix as the effluent is diluted by upstream water; because this WER is due to refractory metal, neither fate processes nor changes in water quality characteristics will affect the WER. When stream flow is higher or lower than design flow, the complete-mix WER will be lower or higher, respectively, than 12, but toxicity will not occur because the concentration of metal will also be lower or higher.

If the eWER and the uWER are strictly additive and if the national CCC is 1 mg/L, the following conclusions are valid when the concentration of the metal in 100 % effluent is less than 40 mg/L and the concentration of the metal in 100 % upstream water is less than 5 mg/L:
1. This metal will not cause acute or chronic toxicity in the upstream water, in 100 % effluent, in the plume, or in downstream water.
2. There is no need for an acute or a chronic mixing zone where a lesser degree of protection is provided.
3. If no mixing zone exists, there is no discontinuity at the edge of a mixing zone where the allowed concentration of metal decreases instantaneously.

These results also apply to partial additivity as long as the concentration of metal does not exceed that allowed by the amount of additivity that exists. It would be more difficult to take into account the portions of the eWER and uWER that are not additive.

The concept of additivity becomes unimportant when the ratios, concentrations of the metals, or WERs are very different. For example, if eWER = 40, uWER = 5, and they are additive, a mixture of 1 % effluent and 99 % upstream water would have a WER of 5.35. Given the reproducibility of toxicity tests and WERs, it would be extremely difficult to distinguish a WER of 5 from a WER of 5.35. In cases of extreme dilution, rather than experimentally determining a WER, it is probably acceptable to use the limiting WER of 5 or to calculate a WER if additivity has been demonstrated.

Traditionally it has been believed that it is environmentally conservative to use a WER determined in upstream water (i.e., the uWER) to derive a site-specific criterion that applies downstream (i.e., that applies to areas that contain effluent). This belief is probably based on the assumption that a larger WER would be obtained in downstream water that contains effluent, but the belief could also be based on the assumption that the uWER is additive. It is possible that in some cases neither assumption is true, which means that using a uWER to derive a downstream site-specific criterion might result in underprotection. It seems likely, however, that WERs determined using downstream water will usually be at least as large as the uWER.

Several kinds of concerns about the use of WERs are actually concerns about additivity:

1. Do WERs need to be determined at higher flows in addition to being determined at design flow?
2. Do WERs need to be determined when two bodies of water mix?
3. Do WERs need to be determined for each additional effluent in a multiple-discharge situation.

In each case, the best use of resources might be to test for additivity of WERs.

Mixing Zones

In the example presented above, there would be no need for a regulatory mixing zone with a reduced level of protection if:

1. The eWER is always 40 and the concentration of the metal in 100 % effluent is always less than 40 mg/L.
2. The uWER is always 5 and the concentration of the metal in 100 % upstream water is always less than 5 mg/L.
3. The WERs are strictly additive.

If, however, the concentration exceeded 40 mg/L in 100 % effluent, but there is some assimilative capacity in the upstream water, a regulatory mixing zone would be needed if the discharge were to be allowed to utilize some or all of the assimilative capacity. The concept of additivity of WERs can be used to calculate the maximum allowed concentration of the metal in the effluent if the eWER and the uWER are strictly additive.

If the concentration of metal in the upstream water never exceeds 0.8 mg/L, the discharger might want to determine how much above 40 mg/L the concentration could be in 100 % effluent. If, for example, the downstream water at the edge of the chronic mixing zone under design-flow conditions consists of 70 % effluent and 30 % upstream water, the WER that would apply at the edge of the mixing zone would be:

$$\frac{70(eWER) + 30(uWER)}{100} = \frac{70(40) + 30(5)}{100} = \frac{2800 + 150}{100} = 29.5 .$$

Therefore, the maximum concentration allowed at this point would be 29.5 mg/L. If the concentration of the metal in the upstream water was 0.8 mg/L, the maximum concentration allowed in 100 % effluent would be 41.8 mg/L because:

$$\frac{70(41.8\ mg/L) + 30(0.8\ mg/L)}{100} = \frac{2926\ mg/L + 24\ mg/L}{100} = 29.5\ mg/L .$$

Because the eWER is 40, if the concentration of the metal in 100 % effluent is 41.8 mg/L, there would be chronic toxicity inside the chronic mixing zone. If the concentration in 100 % effluent is greater than 41.8 mg/L, there would be chronic toxicity past the edge of the chronic mixing zone. Thus even if the eWER and the uWER are taken into account and they are assumed to be completely additive, a mixing zone is necessary if the assimilative capacity of the upstream water is used to allow discharge of more metal.

If the complete-mix downstream water consists of 20 % effluent and 80 % upstream water at design flow, the complete-mix WER would be 12 as calculated above. The complete-mix approach to determining and using downstream WERs would allow a maximum concentration of 12 mg/L at the edge of the chronic mixing zone, whereas the alternative approach resulted in a maximum allowed concentration of 29.5 mg/L. The complete-mix approach would allow a maximum concentration of 16.8 mg/L in the effluent because:

$$\frac{70(16.8\ mg/L) + 30(0.8\ mg/L)}{100} = \frac{1176\ mg/L + 24\ mg/L}{100} = 12\ mg/L .$$

In this example, the complete-mix approach limits the concentration of the metal in the effluent to 16.8 mg/L, even though it is known that as long as the concentration in 100 % effluent is less than 40 mg/L, chronic toxicity will not occur inside or outside the mixing zone. If the WER of 12 is used to derive a site-specific CCC of 12 mg/L that is applied to a site that starts at the edge of the chronic mixing zone and extends all the way across the stream, there would be overprotection at the edge of the chronic mixing zone (because the maximum allowed concentration is 12 mg/L, but a concentration of 29.5 mg/L will not cause chronic toxicity), whereas there would be underprotection on the other side of the stream (because the maximum allowed concentration is 12 mg/L, but concentrations above 5 mg/L can cause chronic toxicity.)

The Experimental Determination of Additivity

Experimental variation makes it difficult to quantify additivity without determining a large number of WERs, but the advantages of demonstrating additivity might be sufficient to make it worth the effort. It should be possible to decide whether the eWER and uWER are strictly additive based on determination of the eWER in 100 % effluent, determination of the uWER in 100 % upstream water, and determination of WERs in 1:3, 1:1, and 3:1 mixtures of the effluent and upstream water, i.e., determination of WERs in 100, 75, 50, 25, and 0 % effluent. Validating models of partial additivity and/or interactions will probably require determination of more WERs and more sophisticated data analysis (see, for example, Broderius 1991).

In some cases chemical measurements or manipulations might help demonstrate that at least some portion of the eWER and/or the uWER is additive:

1. If the difference between the dissolved WER and the total recoverable WER is explained by the difference between the dissolved and total recoverable concentrations, the difference is probably due to particulate refractory metal.
2. If the WERs in different samples of the effluent correlate with the concentration of metal in the effluent, all, or nearly all, of the metal in the effluent is probably nontoxic.
3. A WER that remains constant as the pH is lowered to 6.5 and raised to 9.0 is probably additive.

The concentration of refractory metal is likely to be low in upstream water except during events that increase TSS and/or TOC; the concentration of refractory metal is more likely to be substantial in effluents. Chemical measurements might help identify the percentages of the eWER and the uWER that are due to refractory metal, but again experimental variation will limit the usefulness of chemical measurements when concentrations are low.

Summary

The distinction between the two components of a WER determined using downstream water has the following implications:

1. The magnitude of a WER determined using downstream water will usually depend on the percent effluent in the sample.

2. Insofar as the eWER and uWER are additive, the magnitude of a downstream WER can be calculated from the eWER, the uWER, and the ratio of effluent and upstream water in the downstream water.
3. The derivation and implementation of site-specific criteria should ensure that each component is applied only where it occurs.
   a. Underprotection will occur if, for example, any portion of the eWER is applied to an area of a stream where the effluent does not occur.
   b. Overprotection will occur if, for example, an unnecessarily small portion of the eWER is applied to an area of a stream where the effluent occurs.
4. Even though the concentration of metal might be higher than a criterion in both a regulatory mixing zone and a plume, a reduced level of protection is allowed in a mixing zone, whereas a reduced level of protection is not allowed in the portion of a plume that is not inside a mixing zone.
5. Regulatory mixing zones are necessary if, and only if, a discharger wants to make use of the assimilative capacity of the upstream water.
6. It might be cost-effective to quantify the eWER and uWER, determine the extent of additivity, study variability over time, and then decide how to regulate the metal in the effluent.

Reference

Broderius, S.J. 1991. Modeling the Joint Toxicity of Xenobiotics to Aquatic Organisms: Basic Concepts and Approaches. In: Aquatic Toxicology and Risk Assessment: Fourteenth Volume. (M.A. Mayes and M.G. Barron, eds.) ASTM STP 1124. American Society for Testing and Materials, Philadelphia, PA. pp. 107-127.

Appendix H: Special Considerations Concerning the Determination of WERs with Saltwater Species

1. The test organisms should be compatible with the salinity of the site water, and the salinity of the laboratory dilution water should match that of the site water. Low-salinity stenohaline organisms should not be tested in high-salinity water, whereas high-salinity stenohaline organisms should not be tested in low-salinity water; it is not known, however, whether an incompatibility will affect the WER. If the community to be protected principally consists of euryhaline species, the primary and secondary toxicity tests should use the euryhaline species suggested in Appendix I (or taxonomically related species) whenever possible, although the range of tolerance of the organisms should be checked.
   a. When Method 1 is used to determine cmcWERs at saltwater sites, the selection of test organisms is complicated by the fact that most effluents are freshwater and they are discharged into salt waters having a wide range of salinities. Some state water quality standards require a permittee to meet an LC50 or other toxicity limit at the end of the pipe using a freshwater species. However, the intent of the site-specific and national water quality criteria program is to protect the communities that are at risk. Therefore, freshwater species should not be used when WERs are determined for saltwater sites unless such freshwater species (or closely related species) are in the community at risk. The addition of a small amount of brine and the use of salt-tolerant freshwater species is inappropriate for the same reason. The addition of a large amount of brine and the use of saltwater species that require high salinity should also be avoided when salinity is likely to affect the toxicity of the metal. Salinities that are acceptable for testing euryhaline species can be produced by dilution of effluent with sea water and/or addition of a commercial sea salt or a brine that is prepared by evaporating site water; small increases in salinity are acceptable because the effluent will be diluted with salt water wherever the communities at risk are exposed in the real world. Only as a last resort should freshwater species that tolerate low levels of salinity and are sensitive to metals, such as <u>Daphnia magna</u> and <u>Hyalella azteca</u>, be used.
   b. When Method 2 is used to determine cccWERs at saltwater sites:
      1) If the site water is low-salinity but all the sensitive test organisms are high-salinity stenohaline organisms, a commercial sea salt or a brine that is prepared by evaporating site water may be added in order to increase the salinity to the minimum level that is acceptable to the test organisms; it should be determined whether the

salt or brine reduces the toxicity of the metal and thereby increases the WER.

2) If the site water is high-salinity, selecting test organisms should not be difficult because many of the sensitive test organisms are compatible with high-salinity water.

2. It is especially important to consider the availability of test organisms when saltwater species are to be used, because many of the commonly used saltwater species are not cultured and are only available seasonally.

3. Many standard published methodologies for tests with saltwater species recommend filtration of dilution water, effluent, and/or test solutions through a 37-μm sieve or screen to remove predators. Site water should be filtered only if predators are observed in the sample of the water because filtration might affect toxicity. Although recommended in some test methodologies, ultraviolet treatment is often not needed and generally should be avoided.

4. If a natural salt water is to be used as the laboratory dilution water, the samples should probably be collected at slack high tide ($\pm$ 2 hours). Unless there is stratification, samples should probably be taken at mid-depth; however, if a water quality characteristic, such as salinity or TSS, is important, the vertical and horizontal definition of the point of sampling might be important. A conductivity meter, salinometer, and/or transmissometer might be useful for determining where and at what depth to collect the laboratory dilution water; any measurement of turbidity will probably correlate with TSS.

5. The salinity of the laboratory dilution water should be within $\pm$ 10 percent or 2 mg/L (whichever is higher) of that of the site water.

Appendix I: Suggested Toxicity Tests for Determining WERs for Metals

Selecting primary and secondary toxicity tests for determining WERs for metals should take into account the following:

1. WERs determined with more sensitive tests are likely to be larger than WERs determined with less sensitive tests (see Appendix D). Criteria are derived to protect sensitive species and so WERs should be derived to be appropriate for sensitive species. The appropriate regulatory authority will probably accept WERs derived with less sensitive tests because such WERs are likely to provide at least as much protection as WERs determined with more sensitive tests.
2. The species used in the primary and secondary tests **must** be in different orders and should include a vertebrate and an invertebrate.
3. The test organism (i.e., species and life stage) should be readily available throughout the testing period.
4. The chances of the test being successful should be high.
5. The relative sensitivities of test organisms vary substantially from metal to metal.
6. The sensitivity of a species to a metal usually depends on both the life stage and kind of test used.
7. Water quality characteristics might affect chronic toxicity differently than they affect acute toxicity (Spehar and Carlson 1984; Chapman, unpublished; Voyer and McGovern 1991).
8. The endpoint of the primary test in laboratory dilution water should be as close as possible (but **must not** be below) the CMC or CCC to which the WER is to be applied; the endpoint of the secondary test should be as close as possible (and should not be below) the CMC or CCC.
9. Designation of tests as acute and chronic has no bearing on whether they may be used to determine a cmcWER or a cccWER.

The suggested toxicity tests should be considered, but the actual selection should depend on the specific circumstances that apply to a particular WER determination.

Regardless of whether test solutions are renewed when tests are conducted for other purposes, if the concentrations of dissolved metal and dissolved oxygen remain acceptable when determining WERs, tests whose duration is not longer than 48 hours may be static tests, whereas tests whose duration is longer than 48 hours **must** be renewal tests. If the concentration of dissolved metal and/or the concentration of dissolved oxygen does not remain acceptable, the test solutions **must** be renewed every 24 hours. If one test in a pair of side-by-side tests is a renewal test, both of the tests **must** be renewed on the same schedule.

Appendix H should be read if WERs are to be determined with saltwater species.

Suggested Tests[1] for Determining cmcWERs and cccWERs[2].
(Concentrations are to be measured in all tests.)

Metal	Water[3]	cmcWERs[4]		cccWERs[4]	
Aluminum	FW	DA	X	CDC	X
Arsenic(III)	FW	DA	GM	CDC	FMC
	SW	BM	CR	MYC	BM
Cadmium	FW	DA	SL[5] or FM	CDC	FMC
	SW	MY	CR	MYC	X
Chrom(III)	FW	GM	SL or DA	FMC	CDC
Chrom(VI)	FW	DA	GM	CDC	GM
	SW	MY	NE	MYC	NEC
Copper	FW	DA	FM or GM	CDC	FM
	SW	BM	AR	BMC	AR
Lead	FW	DA	GM	CDC	X
	SW	BM	MYC	MYC	X
Mercury	FW	DA	GM	Y	Y
	SW	MY	BM	Y	Y
Nickel	FW	DA	FX	CDC	FMC
	SW	MY	BM	MYC	BMC
Selenium	FW	Y	Y	Y	Y
	SW	CR	MYC	MYC	X
Silver	FW	DA	FMC	CDC	FMC
	SW	BM	CR	MYC	BMC
Zinc	FW	DA	FM	CDC	FMC
	SW	BM	MY	MYC	BMC

[1] The description of a test specifies not only the test species and the duration of the test but also the life stage of the species and the adverse effect(s) on which the endpoint is to be based.

[2] Some tests that are sensitive and are used in criteria documents are not suggested here because the chances of the test organisms being available and the test being successful might be low. Such tests may be used if desired.

[3] FW = Fresh Water; SW = Salt Water.

[4] Two-letter codes are used for acute tests, whereas codes for chronic tests contain three letters and end in "C". One-letter codes are used for comments.

[5] In acute tests on cadmium with salmonids, substantial numbers of fish usually die after 72 hours. Also, the fish are sensitive to disturbance, and it is sometimes difficult to determine whether a fish is dead or immobilized.

ACUTE TESTS

AR. A 48-hr EC50 based on mortality and abnormal development from a static test with embryos and larvae of sea urchins of a species in the genus Arbacia (ASTM 1993a) or of the species Strongylocentrotus purpuratus (Chapman 1992).

BM. A 48-hr EC50 based on mortality and abnormal larval development from a static test with embryos and larvae of a species in one of four genera (Crassostrea, Mulinia, Mytilus, Mercenaria) of bivalve molluscs (ASTM 1993b).

CR. A 48-hr EC50 (or LC50 if there is no immobilization) from a static test with Acartia or larvae of a saltwater crustacean; if molting does not occur within the first 48 hours, renew at 48 hours and continue the test to 96 hours (ASTM 1993a).

DA. A 48-hr EC50 (or LC50 if there is no immobilization) from a static test with a species in one of three genera (Ceriodaphnia, Daphnia, Simocephalus) in the family Daphnidae (U.S. EPA 1993a; ASTM 1993a).

FM. A 48-hr LC50 from a static test at 25°C with fathead minnow (Pimephales promelas) larvae that are 1 to 24 hours old (ASTM 1993a; U.S. EPA 1993a). The embryos **must** be hatched in the laboratory dilution water, except that organisms to be used in the site water may be hatched in the site water. The larvae **must not** be fed before or during the test and at least 90 percent **must** survive in laboratory dilution water for at least six days after hatch.

Note: The following 48-hr LC50s were obtained at a hardness of 50 mg/L with fathead minnow larvae that were 1 to 24 hours old. The metal was measured using the total recoverable procedure (Peltier 1993):

Metal	LC50 (µg/L)
Cadmium	13.87
Copper	6.33
Zinc	100.95

FX. A 96-hr LC50 from a renewal test (renew at 48 hours) at 25°C with fathead minnow (Pimephales promelas) larvae that are 1 to 24 hours old (ASTM 1993a; U.S. EPA 1993a). The embryos **must** be hatched in the laboratory dilution water, except that organisms to be used in the site water may be hatched in the site water. The larvae **must not** be fed before or during the test and at least 90 percent **must** survive in laboratory dilution water for at least six days after hatch.

Note: A 96-hr LC50 of 188.14 µg/L was obtained at a hardness of 50 mg/L in a test on nickel with fathead minnow larvae that were 1 to 24 hours old. The metal was measured using the total recoverable procedure (Peltier 1993). A 96-hr LC50 is used for nickel because substantial mortality occurred after 48 hours in the test on nickel, but not in the tests on cadmium, copper, and zinc.

GM. A 96-hr EC50 (or LC50 if there is no immobilization) from a renewal test (renew at 48 hours) with a species in the genus Gammarus (ASTM 1993a).

MY. A 96-hr EC50 (or LC50 if there is no immobilization) from a renewal test (renew at 48 hours) with a species in one of two genera (Mysidopsis, Holmesimysis [nee Acanthomysis]) in the family Mysidae (U.S. EPA 1993a; ASTM 1993a). Feeding is required during all acute and chronic tests with mysids; for determining WERs, mysids should be fed four hours before the renewal at 48 hours and minimally on the non-renewal days.

NE. A 96-hr LC50 from a renewal test (renew at 48 hours) using juvenile or adult polychaetes in the genus Nereidae (ASTM 1993a).

SL. A 96-hr EC50 (or LC50 if there is no immobilization) from a renewal test (renew at 48 hours) with a species in one of two genera (Oncorhynchus, Salmo) in the family Salmonidae (ASTM 1993a).

CHRONIC TESTS

BMC. A 7-day IC25 from a survival and development renewal test (renew every 48 hours) with a species of bivalve mollusc, such as a species in the genus Mulinia. One such test has been described by Burgess et al. 1992. [Note: When determining WERs, sediment **must not** be in the test chamber.] [Note: This test has not been widely used.]

CDC. A 7-day IC25 based on reduction in survival and/or reproduction in a renewal test with a species in the genus Ceriodaphnia in the family Daphnidae (U.S. EPA 1993b). The test solutions **must** be renewed every 48 hours. (A 21-day life-cycle test with Daphnia magna is also acceptable.)

FMC. A 7-day IC25 from a survival and growth renewal test (renew every 48 hours) with larvae (≤ 48-hr old) of the fathead minnow (Pimephales promelas) (U.S. EPA 1993b). When determining WERs, the fish **must** be fed four hours before each renewal and minimally during the non-renewal days.

MYC. A 7-day IC25 based on reduction in survival, growth, and/or reproduction in a renewal test with a species in one of two genera (Mysidopsis, Holmesimysis [nee Acanthomysis]) in the family Mysidae (U.S. EPA 1993c). Mysids **must** be fed during all acute and chronic tests; when determining WERs, they **must** be fed four hours before each renewal. The test solutions **must** be renewed every 24 hours.

NEC. A 20-day IC25 from a survival and growth renewal test (renew every 48 hours) with a species in the genus Neanthes (Johns et al. 1991). [Note: When determining WERs, sediment **must not** be in the test chamber.] [Note: This test has not been widely used.]

COMMENTS

X. Another sensitive test cannot be identified at this time, and so other tests used in the criteria document should be considered.

Y. Because neither the CCCs for mercury nor the freshwater criterion for selenium is based on laboratory data concerning toxicity to aquatic life, they cannot be adjusted using a WER.

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U.S. EPA. 1993b. Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms. Third Edition. EPA/600/4-91/002. National Technical Information Service, Springfield, VA.

U.S. EPA. 1993c. Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms. Second Edition. EPA/600/4-91/003. National Technical Information Service, Springfield, VA.

Voyer, R.A., and D.G. McGovern. 1991. Influence of Constant and Fluctuating Salinity on Responses of Mysidopsis bahia Exposed to Cadmium in a Life-Cycle Test. Aquatic Toxicol. 19:215-230.

Appendix J: Recommended Salts of Metals

The following salts are recommended for use when determining a WER for the metal listed. If available, a salt that meets American Chemical Society (ACS) specifications for reagent-grade should be used.

Aluminum
*Aluminum chloride 6-hydrate: $AlCl_3 \bullet 6H_2O$
Aluminum sulfate 18-hydrate: $Al_2(SO_4)_3 \bullet 18H_2O$
Aluminum potassium sulfate 12-hydrate: $AlK(SO_4)_2 \bullet 12H_2O$

Arsenic(III)
*Sodium arsenite: $NaAsO_2$

Arsenic(V)
Sodium arsenate 7-hydrate, dibasic: $Na_2HAsO_4 \bullet 7H_2O$

Cadmium
Cadmium chloride 2.5-hydrate: $CdCl_2 \bullet 2.5H_2O$
Cadmium sulfate hydrate: $3CdSO_4 \bullet 8H_2O$

Chromium(III)
*Chromic chloride 6-hydrate (Chromium chloride): $CrCl_3 \bullet 6H_2O$
*Chromic nitrate 9-hydrate (Chromium nitrate): $Cr(NO_3)_3 \bullet 9H_2O$
Chromium potassium sulfate 12-hydrate: $CrK(SO_4)_2 \bullet 12H_2O$

Chromium(VI)
Potassium chromate: K_2CrO_4
Potassium dichromate: $K_2Cr_2O_7$
*Sodium chromate 4-hydrate: $Na_2CrO_4 \bullet 4H_2O$
Sodium dichromate 2-hydrate: $Na_2Cr_2O_7 \bullet 2H_2O$

Copper
*Cupric chloride 2-hydrate (Copper chloride): $CuCl_2 \bullet 2H_2O$
Cupric nitrate 2.5-hydrate (Copper nitrate): $Cu(NO_3)_2 \bullet 2.5H_2O$
Cupric sulfate 5-hydrate (Copper sulfate): $CuSO_4 \bullet 5H_2O$

Lead
*Lead chloride: $PbCl_2$
Lead nitrate: $Pb(NO_3)_2$

Mercury
Mercuric chloride: $HgCl_2$
Mercuric nitrate monohydrate: $Hg(NO_3)_2 \bullet H_2O$
Mercuric sulfate: $HgSO_4$

Nickel
*Nickelous chloride 6-hydrate (Nickel chloride): $NiCl_2 \bullet 6H_2O$
*Nickelous nitrate 6-hydrate (Nickel nitrate): $Ni(NO_3)_2 \bullet 6H_2O$
Nickelous sulfate 6-hydrate (Nickel sulfate): $NiSO_4 \bullet 6H_2O$

Selenium(IV)
*Sodium selenite 5-hydrate: $Na_2SeO_3 \bullet 5H_2O$

Selenium(VI)
*Sodium selenate 10-hydrate: $Na_2SeO_4 \bullet 10H_2O$

Silver
Silver nitrate: $AgNO_3$
(Even if acidified, standards and samples containing silver **must** be in amber containers.)

Zinc
Zinc chloride: $ZnCl_2$
*Zinc nitrate 6-hydrate: $Zn(NO_3)_2 \bullet 6H_2O$
Zinc sulfate 7-hydrate: $ZnSO_4 \bullet 7H_2O$

*Note: ACS reagent-grade specifications might not be available for this salt.

No salt should be used until information concerning the safety and handling of that salt has been read.

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DUE TO RESOURCE LIMITATIONS, ONLY ONE (1) COPY OF EACH DOCUMENT CAN BE PROVIDED TO A REQUESTOR.

TITLE	CHECK DOCUMENT REQUESTED
1. **Water Quality Standards Regulation, Part II, Environmental Protection Agency, Federal Register, November 8, 1983** *Regulations that govern the development, review, revision and approval of water quality standards under Section 303 of the Clean Water Act.*	
2. **Water Quality Standards Handbook, Second Edition, September 1993** *Contains guidance issued to date in support of the Water Quality Standards Regulation.*	
• **Office of Water Policy and Technical Guidance on Interpretation and Implementation of Aquatic Life Metals Criteria, EPA 822/F-93-009, October 1993** *This memorandum transmits Office of Water policy and guidance on the interpretation and implementation of aquatic life metals criteria. It covers aquatic life criteria, total maximum daily loads permits, effluent monitoring, compliance and ambient monitoring.*	
3. **Water Quality Standards for the 21st Century, 1989** *Summary of the proceedings from the first National Conference on water quality standards held in Dallas, Texas, March 1-3, 1989.*	
4. **Water Quality Standards for the 21st Century, 1991** *Summary of the proceedings from the second National Conference on water quality standards held in Arlington, Virginia, December 10-12, 1990.*	
5. **Compilation of Water Quality Standards for Marine Waters, November 1982** *Consists of marine water quality standards required by Section 304(a)(6) of the Clean Water Act. The document identifies marine water quality standards, the specific pollutants associated with such water quality standards and the particular waters to which such water quality standards apply. The compilation should not in any way be construed as Agency opinion as to whether the waters listed are marine waters within the meaning of Section 301(h) of the Clean Water Act or whether discharges to such waters are qualified for a Section 301(h) modification.*	

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6. Technical Support Manual: Waterbody Surveys and Assessments for Conducting Use Attainability Analyses, November 1983 *Contains technical guidance to assist States in implementing the revised water quality standards regulation (48 FR 51400, November 8, 1983). The guidance assists States in answering three key questions:* *a. What are the aquatic protection uses currently being achieved in the waterbody?* *b. What are the potential uses that can be attained based on the physical, chemical and biological characteristics of the waterbody?* *c. What are the causes of any impairment of the uses?*	
7. Technical Support Manual: Waterbody Surveys and Assessments for Conducting Use Attainability Analyses, Volume II: Estuarine Systems *Contains technical guidance to assist States in implementing the revised water quality standards regulation (48 FR 51400, November 8, 1983). This document addresses the unique characteristics of estuarine systems and supplements the Technical Support Manual: Waterbody Summary and Assessments for Conducting Use Attainability Analyses (EPA, November 1983).*	
8. Technical Support Manual: Waterbody Surveys and Assessments for Conducting Use Attainability Analyses, Volume III: Lake Systems, November 1984 *Contains technical guidance to assist States in implementing the revised water quality standards regulation (48 FR 51400 November 8, 1983). The document addresses the unique characteristics of lake systems and supplements two additional guidance documents: Technical Support Manual: Waterbody Survey and Assessments for Conducting Use Attainability Analyses EPA, (November 1983) and Technical Support Manual: Waterbody Surveys and Assessments for Conducting Use Attainability Analyses, Vol II: Estuarine Systems.*	
9. Health Effects Criteria for Marine Recreational Waters, EPA 600/1-80-031, August 1983 *This report presents health effects quality criteria for marine recreational waters and a recommendation for a specific criterion. The criteria were among those developed using data collected from an extensive in-house extramural microbiological research program conducted by the U.S. EPA over the years 1972-1979.*	
10. Health Effects Criteria for Fresh Recreational Waters, EPA 660/1-84-004, August 1984 *This report presents health effects criteria for fresh recreational waters and a criterion for the quality of the bathing water based upon swimming - associated gastrointestinal illness. The criterion was developed from data obtained during a multi-year freshwater epidemiological-microbiological research program conducted at bathing beaches near Erie, Pennsylvania and Tulsa, Oklahoma. Three bacterial indications of fecal pollution were used to measure the water quality: E. Coli, enterococci and fecal coliforms.*	
11. Introduction to Water Quality Standards, EPA 440/5-88-089, September 1988 *A primer on the water quality standards program written in question and answer format. The publication provides general information about various elements of the water quality standards program.*	
12. Ambient Water Quality Criteria for Bacteria - 1986 EPA 440/5-84-002 *This document contains bacteriological water quality criteria. The recommended criteria are based on an estimate of bacterial indicator counts and gastro-intestinal illness rates.*	

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TITLE	**CHECK DOCUMENT REQUESTED**
13. Test Methods for Escherichia Coil and Enterococci; In Water by the Membrane Filter Procedure, EPA 600/4-85/076, 1985 *Contains methods used to measure the bacteriological densities of E. coli and enterococci in ambient waters. A direct relationship between the density of enterococci and E. coli in water and the occurrence of swimming - associated gastroenteritis has been established through epidemiological studies of marine and fresh water bathing beaches. These studies have led to the development of criteria which can be used to establish recreational water standards based on recognized health effects-water quality relationships.*	
14. Twenty-Six Water Quality Standards Criteria Summaries, September 1988 *These documents contain twenty-six summaries of State/Federal criteria. Twenty-six summaries have been compiled which contain information extracted from State water quality standards. Titles of the twenty-six documents are: Acidity-Alkalinity, Antidegradation, Arsenic, Bacteria, Cadmium, Chromium, Copper, Cyanide, Definitions, Designated Uses, Dissolved Oxygen, Dissolved Solids, General Provisions, Intermittent Streams, Iron, Lead, Mercury, Mixing Zones, Nitrogen-Ammonia/Nitrate/Nitrite, Organics, Other Elements, Pesticides, Phosphorus, Temperature, Turbidity, and Zinc.*	
15. Fifty-Seven State Water Quality Standards Summaries, September 1988 *Contains fifty-seven individual summaries of State water quality standards. Included in each summary is the name of a contact person, use classifications of water bodies, mixing zones, antidegradation policies and other pertinent information.*	
16. State Water Quality Standards Summaries, September 1988 (Composite document) *This document contains composite summaries of State water quality standards. The document contains information about use classifications, antidegradation policies and other information applicable to a States' water quality standards.*	
17. Transmittal of Final "Guidance for State Implementation of Water Quality Standards for CWA Section 303(c)(2)(B)", December 12, 1988 *Guidance on State adoption of criteria for priority toxic pollutants. The guidance is designed to help States comply with the 1987 Amendments to the Clean Water Act which requires States to control toxics in water quality standards.*	
18. Chronological Summary of Federal Water Quality Standards Promulgation Actions, January 1993 *This document contains the date, type of action and Federal Register citation for State water quality standards promulgated by EPA. The publication also contains information on Federally promulgated water quality standards which have been withdrawn and replaced with State approved standards.*	
19. Status Report: State Compliance with CWA Section 303(c)(2)(b) as of February 4, 1990 *Contains information on State efforts to comply with Section 303(c)(2)(B) of the Clean Water Act which requires adoption of water quality standards for priority pollutants. The report identifies the States that are compliant as of February 4, 1990, summarizes the status of State actions to adopt priority pollutants and briefly outlines EPA's plan to federally promulgate standards for noncompliant States.*	
20. Water Quality Standards for Wetlands: National Guidance, July 1990 *Provides guidance for meeting the priority established in the FY 1991 Agency Operating Guidance to develop water quality standards for wetlands during the FY 1991-1993 triennium. By the end of FY 1993, States are required as a minimum to include wetlands in the definition of "State waters," establish beneficial uses for wetlands, adopt existing narrative and numeric criteria for wetlands, adopt narrative biological criteria for wetlands and apply antidegradation policies to wetlands.*	

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21. Reference Guide for Water Quality Standards for Indian Tribes, January 1990 *Booklet provides an overview of the water quality standards program. Publication is designed primarily for Indian Tribes that wish to qualify as States for the water quality standards program. The booklet contains program requirements and a list of reference sources.*	
22. Developing Criteria to Protect Our Nation's Waters, EPA, September 1990 (Pamphlet) *Pamphlet which briefly describes the water quality standards program and its relationship to water quality criteria, sediment criteria and biological criteria.*	
23. Water Quality Standards for the 21st Century, EPA 823-R-92-009, December 1992 *Summary of the proceedings from the Third National Conference on Water Quality Standards held in Las Vegas, Nevada, August 31-September 3, 1992*	
24. Biological Criteria: National Program Guidance for Surface Waters, EPA-440/5-90-004, April 1990 *This document provides guidance for development and implementation of narrative biological criteria.*	
25. Amendments to the Water Quality Standards Regulation that Pertain to Standards on Indian Reservations - Final Rule. Environmental Protection Agency, Federal Register, December 12, 1991 *This final rule amends the water quality standards regulation by adding: 1) procedures by which an Indian Tribe may qualify for treatment as a State for purposes of the water quality standards and 401 certification programs and 2) a mechanism to resolve unreasonable consequences that may arise when an Indian Tribe and a State adopt different water quality standards on a common body of water.*	
26. Guidance on Water Quality Standards and 401 Certification Programs Administered by Indian Tribes, December 31, 1991 *This guidance provides procedures for determining Tribal eligibility and supplements the final rule "Amendments to the Water Quality Standards Regulation that Pertain to Standards on Indian Reservations".*	
27. Water Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants; State's Compliance - Final Rule, Environmental Protection Agency, Federal Register, December 22, 1992 *This regulation promulgates for 14 States, the chemical specific, numeric criteria for priority toxic pollutants necessary to bring all States into compliance with the requirements of Section 303(c)(2)(B) of the Clean Water Act. Staates determined by EPA to fully comply with Section 303(c)(2)(B) requirements are not affected by this rule.*	
28. Interim Guidance on Determinations and Use of Water-Effect Ratios for Metals, EPA 823-B-94-001, February 1994 *This guidance contains specific information on procedures for developing water-effect ratios.*	

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WATERSHED MODELING SECTION TITLE	CHECK DOCUMENT REQUESTED
1. **Guidance for Water Quality-based Decisions: The TMDL Process, EPA 440/4-91-001, April 1991** *This document defines and clarifies the requirements under Section 303(d) of the Clean Water Act. Its purpose is to help State water quality program managers understand the application of total maximum daily loads (TMDLs) through an integrated, basin-wide approach to controlling point and nonpoint source pollution. The document describes the steps that are involved in identifying and prioritizing impaired waters and developing and implementing TMDLs for waters listed under Section 303(d).* **Contact: Don Brady (202) 260-5368**	
2. **Technical Guidance Manual for Performing Waste Load Allocations - Book II Streams and Rivers - Chapter 1 Biochemical Oxygen Demand/Dissolved Oxygen, EPA 440/4-84-020, September 1983** *This chapter presents the underlying technical basis for performing WLA and analysis of BOD/DO impacts. Mathematical models to calculate water quality impacts are discussed, along with data needs and data quality.* **Contact: Bryan Goodwin (202) 260-1308**	
3. **Technical Guidance Manual for Performing Waste Load Allocations - Book II Streams and Rivers - Chapter 2 Nutrient/Eutrophication Impacts, EPA 440/4-84-021, November 1983** *This chapter emphasizes the effect of photosynthetic activity stimulated by nutrient discharges on the DO of a stream or river. It is principally directed at calculating DO concentrations using simplified estimating techniques.* **Contact: Bryan Goodwin (202) 260-1308**	
4. **Technical Guidance Manual for Performing Waste Load Allocations - Book II Streams and Rivers - Chapter 3 Toxic Substances, EPA 440/4-84-022, June 1984** *This chapter describes mathematical models for predicting toxicant concentrations in rivers. It covers a range of complexities, from dilution calculations to complex, multi-dimensional, time-varying computer models. The guidance includes discussion of background information and assumptions for specifying values.* **Contact: Bryan Goodwin (202) 260-1308**	

STANDARDS & APPLIED SCIENCE DIVISION/EXPOSURE ASSESSMENT BRANCH	
WATERSHED MODELING SECTION TITLE	CHECK DOCUMENT REQUESTED
5. **Technical Guidance Manual for Performing Waste Load Allocations - Simplified Analytical Method for Determining NPDES Effluent Limitations for POTWs Discharging into Low-Flow Streams** *This document describes methods primarily intended for "desk top" WLA investigations or screening studies that use available data for streamflow, effluent flow, and water quality. It is intended for circumstances where resources for analysis and data acquisition are relatively limited.* **Contact: King Boynton (202) 260-7013**	
6. **Technical Guidance Manual for Performing Waste Load Allocations - Book IV Lakes and Impoundments - Chapter 2 Nutrient/Eutrophication Impacts, EPA 440/4-84-019, August 1983** *This chapter discusses lake eutrophication processes and some factors that influence the performance of WLA analysis and the interpretation of results. Three classes of models are discussed, along with the application of models and interpretation of resulting calculations. Finally, the document provides guidance on monitoring programs and simple statistical procedures.* **Contact: Bryan Goodwin (202) 260-1308**	
7. **Technical Guidance Manual for Performing Waste Load Allocations - Book IV Lakes, Reservoirs and Impoundments - Chapter 3 Toxic Substances Impact, EPA 440/4-87-002, December 1986** *This chapter reviews the basic principles of chemical water quality modeling frameworks. The guidance includes discussion of assumptions and limitations of such modeling frameworks, as well as the type of information required for model application. Different levels of model complexity are illustrated in step-by-step examples.* **Contact: Bryan Goodwin (202) 260-1308**	
8. **Technical Guidance Manual for Performing Waste Load Allocations - Book VI Design Conditions - Chapter 1 Stream Design Flow for Steady-State Modeling, EPA 440/4-87-004, September 1986** *Many state water quality standards (WQS) specify specific design flows. Where such design flows are not specified in WQS, this document provides a method to assist in establishing a maximum design flow for the final chronic value (FCV) of any pollutant.* **Contact: Bryan Goodwin (202) 260-1308**	
9. **Final Technical Guidance on Supplementary Stream Design Conditions for Steady State Modeling, December 1988** *WQS for many pollutants are written as a function of ambient environmental conditions, such as temperature, pH or hardness. This document provides guidance on selecting values for these parameters when performing steady-state WLAs.* **Contact: Bryan Goodwin (202) 260-1308**	
10. **Technical Guidance Manual for Performing Waste Load Allocations - Book VII: Permit Averaging, EPA 440/4-84-023, July 1984** *This document provides an innovative approach to determining which types of permit limits (daily maximum, weekly, or monthly averages) should be specified for the steady-state model output, based on the frequency of acute criteria violations.* **Contact: Bryan Goodwin (202) 260-1308**	
11. **Water Quality Assessment: A Screening Procedure for Toxic and Conventional Pollutants in Surface and Ground Water - Part I - EPA 600/6-85-022a, September 1985** *This document provides a range of analyses to be used for water quality assessment. Chapters include consideration of aquatic fate of toxic organic substances, waste loading calculations, rivers and streams, impoundments, estuaries, and groundwater.* **Contact: Bryan Goodwin (202) 260-1308**	

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12. Water Quality Assessment: A Screening Procedure for Toxic and Conventional Pollutants in Surface and Ground Water - Part II - EPA 600/6-85-022b, September 1985 *This document provides a range of analyses to be used for water quality assessment. Chapters include consideration of aquatic fate of toxic organic substances, waste loading calculations, rivers and streams, impoundments, estuaries, and ground water.* **Contact: Bryan Goodwin (202) 260-1308**	
13. Handbook - Stream Sampling for Waste Load Allocation Applications, EPA 625/6-86/013, September 1986 *This handbook provides guidance in designing stream surveys to support modeling applications for waste load allocations. It describes the data collection process for model support, and it shows how models can be used to help design stream surveys. In general, the handbook is intended to educate field personnel on the relationship between sampling and modeling requirements.* **Contact: Bryan Goodwin (202) 260-1308**	
14. EPA's Review and Approval Procedure for State Submitted TMDLs/WLAs, March 1986 *The step-by-step procedure outlined in this guidance addresses the administrative (i.e., non-technical) aspects of developing TMDLs/WLAs and submitting them to EPA for review and approval. It includes questions and answers to focus on key issues, pertinent sections of WQM regulations and the CWA, and examples of correspondence.* **Contact: Bryan Goodwin (202) 260-1308**	
15. Guidance for State Water Monitoring and Wasteload Allocation Programs, EPA 440/4-85-031, October 1985 *This guidance is for use by States and EPA Regions in developing annual section 106 and 205(j) work programs. The first part of the document outlines the objectives of the water monitoring program to conduct assessments and make necessary control decisions. The second part describes the process of identifying and calculating total maximum daily loads and waste load allocations for point and nonpoint sources of pollution.* **Contact: King Boynton (202) 260-7013**	
16. Technical Guidance Manual for Performing Waste Load Allocations Book III Estuaries - Part 1 - Estuaries and Waste Load Allocation Models, EPA 823-R-92-002, May 1990 *This document provides technical information and policy guidance for preparing estuarine WLA. It summarizes the important water quality problems, estuarine characteristics, and the simulation models available for addressing these problems.* **Contact: Bryan Goodwin (202) 260-1308**	
17. Technical Guidance Manual for Performing Waste Load Allocations Book III Estuaries - Part 2 - Application of Estuarine Waste Load Allocation Models, EPA 823-R-92-003, May 1990 *This document provides a guide to monitoring and model calibration and testing, and a case study tutorial on simulation of WLA problems in simplified estuarine systems.* **Contact: Bryan Goodwin (202) 260-1308**	

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18. **Technical Guidance Manual for Performing Wasteload Allocations-Book III: Estuaries - Part 3 - Use of Mixing Zone Models in Estuarine Wasteload Allocations, EPA 823-R-92-004** *This technical guidance manual describes the initial mixing wastewater in estuarine and coastal environments and mixing zone requirements. The important physical processess that govern the hydrodynamic mixing of aqueous discharges are described, followed by application of available EPA supported mixing zone models to four case study situations.* **Contact: Bryan Goodwin (202) 260-1308**	
19. **Technical Guidance Manual for Performing Wasteload Allocations - Book III - Estuaries - Part 4 - Critical Review of Coastal Embayment and Estuarine Wasteload Allocation Modeling, EPA 823-R-92-005, August 1992** *This document summarizes several historical case studies of model use in one freshwater coastal embayment and a number of estuarine discharge situations.* **Contact: Bryan Goodwin (202) 260-1308**	
20. **Technical Support Document for Water Quality-based Toxics Control, EPA 505/2-90-001, March, 1991** *This document discusses assessment approaches, water quality standards, derivation of ambient criteria, effluent characterization, human health hazard assessment, exposure assessment, permit requirements, and compliance monitoring. An example is used to illustrate the recommended procedures.* **Contact: King Boynton (202) 260-7013**	
21. **Rates, Constants, and Kinetics Formulations in Surface Water Quality Modeling (Second Edition), U.S. EPA 600/3-85/040, June 1985** *This manual serves as a reference on modeling formulations, constants and rates commonly used in surface water quality simulations. This manual also provides a range of coefficient values that can be used to perform sensitivity analyses.* **Contact: Bryan Goodwin (202) 260-1308**	
22. **Dynamic Toxics Waste Load Allocation Model (DYNTOX), User's Manual, September 13, 1985** *A user's manual which explains how to use the DYNTOX model. It is designed for use in wasteload allocation of toxic substances.* **Contact: Bryan Goodwin (202) 260-1308**	
23. **Windows Front-End to SWMM (Storm Water Management Model), EPA 823-C-94-001, February 1994** *A user interface (front-end) to the Storm Water Management Model (SWMM) and supporting documentation is avaiable on diskette. Operating in the Microsoft Windows Environment, this interface simplifies data entry and model set-up.* **Contact: Jerry LaVeck (202) 260-7771**	
24. **Windows Front-End to SWRRBWQ (Simulator for Water Resources in Rural Basins-Water Quality), EPA 823-C-94-002, February 1994** *A user interface (front-end) to the Simulator for Water Resource in Rural Basins-Water Quality model and supporting documentation is available on diskette. Operating in the Microsoft Windows environment, this interface simplifies data entry and model set-up.* Contact: Jerry LaVeck (202) 260-7771	

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25. De Minimis Discharges Study: Report to Congress, U.S. EPA 440/4-91-002, November 1991 *This report to Congress addresses the requirements of Section 516 by identifying potential de minimis discharges and recommends effective and appropriate methods of regulating those discharges.* **Contact: Rich Healy (202) 260-7812**	
26. National Study of Chemical Residues in Fish. Volume I, U.S. EPA 823-R-92-008 a, September 1992 *This report contains results of a screening study of chemical residues in fish taken from polluted waters.* **Contact: Richard Healy (202) 260-7812**	
27. National Study of Chemical Residues in Fish. Volume II. U.S. EPA 823-R-92-008 b, September 1992 *This report contains results of a screening study of chemical residues in fish taken from polluted waters.* **Contact: Richard Healy (202) 260-7812**	

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SEDIMENT CONTAMINATION SECTION TITLE	CHECK DOCUMENT REQUESTED
1. **Sediment Classification Methods Compendium, U.S. EPA, EPA 823-R-92-006, September 1992** *This compendium is an "encyclopedia" of methods that are used to assess chemically contaminated sediments. It contains a description of each method, associated advantages and limitations and existing applications.* **Contact: Beverly Baker (202) 260-7037**	
2. **Managing Contaminated Sediments: EPA Decision-Making Processes, Sediment Oversight Technical Committee, U.S. EPA Report - 506/6-90/002, December, 1990** *This document identifies EPA's current decision-making process (across relevant statutes and programs) for assessing and managing contaminated sediments. Management activities relating to contaminated sediments are divided into the following six categories: finding contaminated sediments, assessment of contaminated sediments, prevention and source controls, remediation, treatment of removed sediments, and disposal of removed sediments.* **Contact: Mike Kravitz (202) 260-7049**	
3. **Contaminated Sediments: Relevant Statutes and EPA Program Activities, Sediment Oversight Technical Committee, U.S. EPA Report - 506/6-90/003, December, 1990** *This document provides information on program office activities relating to contaminated sediment issues, and the specific statutes under which these activities fall. A table containing major laws or agreements relevant to sediment quality issues is included.* **Contact: Mike Kravitz (202) 260-7049**	

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4. **Contaminated Sediments News, U.S. EPA 823-N92-001** *This newsletter, issued periodically, contains information about contaminated sediment issues. Back issues of the newsletter are available.* • **Contact: Beverly Baker (202) 260-7037**	
• **Contaminated Sediments News, Number 1, August 1989**	
• **Contaminated Sediments News, Number 2, April 1990**	
• **Contaminated Sediments News, Number 3, April 1991**	
• **Contaminated Sediments News, Number 4, February 1992**	
• **Contaminated Sediments News, Number 5, April 1992**	
• **Contaminated Sediments News, Number 6, August 1992**	
• **Contaminated Sediments News, Number 7, December 1992**	
• **Contaminated Sediments News, Number 8, May 1993**	
• **Contaminated Sediment News, Number 9, August 1993**	
• **Contaminated Sediment News, Number 10, December 1993**	
5. **Proceedings of the EPA's Contaminated Sediment Management Forum, U.S. EPA, Report 823-R-92-007, September 1992** *This report summarizes the proceedings of three EPA sponsored forums designed to obtain input on EPA's Contaminated Sediment Management Strategy.* **Contact: Beverly Baker (202) 260-7037**	
6. **Selecting Remediation Techniques for Contaminated Sediment, U.S. EPA 823-B93-001, June 1993** *This planning guide assists federal-State remedial managers, local agencies, private cleanup companies and supporting contractors in remedial decision-making process at contaminated sediment sites.* **Contact: Beverly Baker (202) 260-7037**	
7. **Questions and Answers About Contaminated Sediments, U.S. EPA 823-F-93-009, May 1993** *This general pamphlet highlights what sediments are, how they are contaminated and what can be done.* **Contact: Beverly Baker (202) 260-7037**	
8. **Tiered Testing Issues for Freshwater and Marine Sediments, U.S. EPA 823-R93-001, February 1993, Proceedings of A Workshop Held in Washington, DC, September 16-18, 1992.** *This report summarizes the proceedings of the workshop sponsored by the Office of Water and Office of Research and Development. The workshop was held to provide an opportunity for experts in sediment toxicology and EPA to discuss the development of standard freshwater and marine sediment bioassay procedures.* **Contact: Thomas Armitage (202) 260-5388**	

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FISH CONTAMINATION SECTION TITLE	**CHECK DOCUMENT REQUESTED**
9. Special Interest Group (SIG) Forum for Fish Consumption, User's Manual, V.1.0., U.S. EPA 822/8-91/001, February 1992 *This user's manual describes various features of the Special Interest Group (SIG) Forum for fish consumption advisotries, bans and risk management. The manual explains how to access the SIG and use its data bases, messags, bulletins and other computer files.* **Contact: Jeff Bigler (202) 260-1305**	
10. Consumption Surveys for Fish and Shellfish, A Review and Analysis of Survey Methods, U.S. EPA-822/R-92-001, February 1992. *This document contains a critical analysis of methods used to determine fish consumption rates of recreational and subsistence fisherment, groups that have the greates potential for exposure to contaminants in fish tissues.* **Contact: Jeff Bigler (202) 260-1305**	
11. Proceedings of the U.S. Environmental Protection Agency's National Technical Workshop "PCBs in Fish Tissue", U.S. EPA/823-R-93-003, September 1993 *This documents summarizes the proceedings of the EPA sponsored workshop held on May 10-11, 1993 in Washington, DC.* **Contact: Rick Hoffman (202) 260-0642**	
12. Guidance for Assessing Chemical Contaminant Data for Use in Risk Advisories, Volume 1: Fish Sampling and Analysis, EPA 823-R-93-002, August 1993 *This document provides detailed technical guidance on methods for sampling and analyzing chemical contaminants in fish and shellfish tissues. It addresses monitoring strategies, selection of fish species and chemical analytes, field and laboratory procedures and data analyses.* **Contact: Jeff Bigler (202) 260-1305**	
13. National Fish Tissue Data Repository User Manual, Version 1.0, EPA 823-B-903-003, November 1993 *The U.S. EPA has developed the National Fish Tissue Data Repository (NFTDR) for collection and storage of fish and shellfish contaminants data. The data repository is part of a large EPA data base system called the Ocean Data Evaluation System (ODES). This manual explains how to access information from the ODES database.* **Contact: Rick Hoffman (202) 260-0642**	
14. National Fish Tissue Data Repository: Data Entry Guide, Version 1.0, EPA 823-B-93-006, November 1993 *The U.S. EPA has developed the National Fish Tissue Data Repository (NFTDR) for collection and storage of fish and shellfish contaminants data. The data repository is part of a larger EPA data base system known as the Ocean Data Evaluation System (ODES). This manual assists State and Federal Agencies in submitting data to the NFTDR.* **Contact: Rick Hoffman (202) 260-0642**	

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Summary of Updates

APPENDIX X

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